



FRAME

FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS

DELIVERABLE D5.2

Develop and/or review
models for the formation of
natural graphite, lithium and
cobalt in Europe.



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FRAME

FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS

Table of Contents

Table of Contents.....	2
Disclaimer	7
Executive summary	8
1 Introduction.....	2
2 Materials and methods.....	4
2.1 Data material and source	4
3 Lithium.....	5
3.1 Properties of Lithium	5
3.2 Lithium minerals	5
3.3 Behaviour and distribution of lithium in geological processes.....	6
3.3.1 Distribution of lithium in rocks.....	6
3.3.2 Behaviour of lithium in geological processes.....	7
3.3.2.1 Metamorphic processes.....	7
3.3.2.2 Magmatic processes.....	8
3.3.2.3 Hydrothermal processes	8
3.4 Model of formation of lithium mineralisation	9
3.4.1 Lithium mineralisation associated with deep processes.....	9
3.4.1.1 Lithium-Cesium-Tantalum Pegmatites.....	9
3.4.1.1.1 Model of granite source	11
3.4.1.1.2 Partial melting model	11
3.4.1.2 Rare metal granites	12
3.4.1.3 Greisens.....	14
3.4.1.4 Lithium-phosphate quartz vein	15
3.4.2 Lithium mineralisation associated with surficial processes.	15
3.4.2.1 Stratiform sedimentary-hydrothermal lithium mineralisation	15
3.4.2.2 Lithium-bearing bauxites.....	18
3.4.2.3 Others non-economic lithium mineralisation types	18
4 Cobalt	19
4.1 Properties of cobalt.....	19



FRAME

FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS

4.2	Cobalt behaviour in ore forming processes and genetic types.	20
4.2.1	Cobalt behaviour in magmatic processes (magmatic Ni-Cu-Co deposits)	20
4.2.2	Cobalt behaviour in hydrothermal processes (sediment-hosted Cu-Co, vein-type and VMS deposits)	22
4.2.1.1	Cobalt behaviour in sediment-hosted Cu-Co deposits.....	22
4.2.1.2	Cobalt behaviour in vein-type deposits (5-element vein deposits)	23
4.2.1.3	Cobalt behaviour in sea floor hydrothermal system (Cu-Zn-Pb VMS deposits)	24
4.2.3	Cobalt behaviour in supergene processes (lateritic Ni-Co deposits)	25
5	Graphite.....	27
5.1	Graphite deposit types, formation and characterization.	27
5.1.1	Scientific classification of graphite and carbonaceous material.....	27
5.1.1.1	Raman spectroscopy	29
5.1.1.2	Carbon isotopes.....	30
5.1.2	Industrial classification of graphite types	31
5.1.2.1	Properties, use and quality requirements.....	32
5.2	Field relationships of graphite deposits.....	33
5.3	Exploration for graphite deposits.....	34
6	Summary and conclusions	36
7	References	39
8	Appendix 1, Overview of partners, contributors, the collected data and its organisation.	48
	Appendix 2 Maps of Lithium cobalt and graphite occurrences	51



FRAME

FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS

Figures

Figure 1 Principe for the construction of the Li-ion battery, where the important materials of the anode and cathode is listed (modified from (Whittingham, 2020).	2
Figure 2 The wheel of metal companionality.....	3
Figure 3: Chemical evolution through a lithium-rich pegmatite group with distance from the granitic source. Modified from London (2008)	11
Figure 4: anatectic model for the generation of pegmatites (barren and Li-rich) and rare-metal granites. Some European mineralisation are given. Modified from Gourcerol et al (2019).	12
Figure 5: Cross sections of various lithium deposits. Lithium-bearing units are identified in red in each section. A) Beauvoir RMG (France) and related stockwork; B) Sepeda pegmatite in Portugal; orange area represents barren pegmatite. C) Cinovec deposit in Czech Republic; D) Jadar Basin in Serbia and location of the jadarite layers; modified from Gourcerol et al (2019) and references enclosed.	13
Figure 6: Block models of mature and immature salars showing the distribution of facies and main hydrological components. In the mature model, extension and recession of the marginal facies as a result of tectonism and climate variation lead to the possibility of dilute waters being transferred into the nucleus. In the immature model, while the marginal conditions have been simplified for clarity, the transmission of dilute waters into the nucleus is also possible. K refers to the hydraulic conductivity of the different units. Modified from Houston et al (2011).	17
Figure 7 Global examples of average Ni and Co grades of some Ni-Cu deposits.....	21
Figure 8 Schematic cross section of intracratonic rift basin and associated SSHC-type Cu-Co deposits. Modified after Hitzman et al., 2010. Schematic cross section of intracratonic rift basin and associated SSHC-type Cu-Co deposits. Modified after Hitzman et al., 2010.	23
Figure 9 Schematic cross section of a typical submarine hydrothermal system. Vertical scale exaggerated. Modified after Hannington, 2014.	25
Figure 10 Schematic laterite profile developed on ultramafic rock with approximate chemical composition on right (modified after Elias 2002).	26
Figure 11 The process of graphite formation from diagenesis to fully crystalline graphite sees (Buseck & Beyssac, 2014) for details.....	28
Figure 12 Raman shift in relation to metamorphic grade in graphite from (Buseck & Beyssac, 2014).	30
Figure 13 The carbon isotope signature in relation to source and process of formation (modified from (Luque et al., 2012)	31
Figure 14 Drill logs showing the typical distribution of graphite rich layers and associated country rock types (from Gautneb et al 2020).....	34
Figure 15 Figures showing the some of the steps in graphite exploration a) airborne geophysics b) and c) ground geophysics. Blue arrows show indicate graphite lenses along profile 1-3. From (Gautneb et al., 2020).	35



FRAME

FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS

Tables

Table 1 : Most common Li-bearing minerals. Data source: IMA.....	6
Table 2: Average lithium concentration for various terrestrial reservoirs, igneous and sedimentary rocks and soils. Data from: a)(Li, 2000); b) (Teng et al., 2004); c) (Taylor & McLennan, 2008); d) (Ling et al., 2018).	7
Table 3: Pegmatite classification according to(Černý & Ercit, 2005). Economic lithium-pegmatites are in bold	10
Table 4 Important cobalt minerals and cobalt-containing minerals in ore deposits.	19
Table 5 Distinction of graphite, semi graphite, meta anthracite and anthracite with XRD and vitrinite reflectance (compiled from (Kwiecińska & Petersen, 2004).	29
Table 6 Traditional trade products of graphite.....	33
Table 7 List of Partners/countries, MREG members and individuals that delivered data to WP5.	48
Table 8 Data requested for the occurrences of Li, Co and graphite in Europe.....	49
Table 9 The number of occurrences per country and element.	50



FRAME

FORECASTING AND ASSESSING EUROPE'S
STRATEGIC RAW MATERIALS NEEDS

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Executive summary

This report gives a summary of models for the formation and the processes that are operating during the formation of lithium, cobalt and graphite deposits. The aim of this report is to provide support material to the deliverables D5.1 and D.5.3 and D.5.6 of the work package 5 of the FRAME project. The differences and complexities of the geology between lithium cobalt and graphite is very large, this is also reflected in the content and overall layout of this report. This report is made as concise as possible, however the nature of the topic are such that certain level of geological background is needed to fully appreciate the descriptions.

Lithium

There are about 120 different lithium bearing minerals, 12 of these are the most common and, of these, spodumene (containing 8.03 wt.% Li_2O) is the most common. The following types of Lithium occurrences is described in this report:

Lithium cesium tantalum (LCT) pegmatites; Several models are proposed in the literature for the formation of these type of mineralisation and we give review of the the granitic source and partial melting model, and both require strict geological setting and processes to occur. Compared to the common nature of pegmatites in general, lithium bearing pegmatites must be regarded as rare. Typical deposits of this type in EU are: Spodumene-bearing pegmatites from the Kaustinen province (Finland), from the Barroso-Alvão pegmatite field (Portugal), from the Lalín-Forcarei pegmatite field (Spain) and from the Eastern Alps (Austria).

Li-rich Rare metal granites; Rare metal granites are peraluminous granites that are enriched in various types of metals. They are believed to be produced by melting of sedimentary rocks. They can contain from 0.5-1.0 % Li_2O . The lithium bearing minerals are typically phosphates and phyllosilicates. The rare metal granites usually represents much larger volumes when compared to pegmatites. Typical deposits of this type in EU are encountered in the rare-metal granite belt of the French Massif central (Beauvoir, Montebbras, Richemont) and in Portugal (Argemela).

Greisen; Greisen are hydrothermally altered rocks that are associated with granitic intrusions. Lithium-rich greisen are generally developed within rare-metal granite. Typical Li_2O grades are about 0.4%. The composition of the granitic precursor seems to be important for the enrichment of Lithium in the associated greisen. Large Lithium-rich greisens are located along the Czech-German border (Cinovec, Zinnwald, Sadisdorf, Krásno).

Lithium phosphate quartz veins; In the final stage of crystallization of rare metal granites, fluids rich in silica, phosphorous, lithium and fluorine can be formed. The Argemela mine deposit in Portugal is the present-day best known example. Other occurrences are known in Portugal and France (Montebbras).

Stratiform sedimentary-hydrothermal lithium mineralisation; This type of deposits represents localities where there have been a flux of lithium bearing fluids of a long period of time. Usually



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STRATEGIC RAW MATERIALS NEEDS

some form of depression or sedimentary basin are the traps for lithiums in these type of occurrences. These type of occurrences have the following sub types:

Clay-type: Several clay minerals can be lithium bearing, the weathering conditions and host rock compositions determines the clay mineral composition and its lithium content. Typical lithium contents are 2000-3000 ppm. EU Potential for this type of deposit should be significant but has never been assessed.

Brines: Brines are defined as hypersaline solutions with 1.7 to 2x times that of seawater. They can be related to geothermal processes or non geothermal. Lithium brine occurrences tend to be very large and usually form large salt type deposits (salars). Typical lithium contents are in the order < 350 ppm/L. Geothermal Lithium-rich brines are outside the focus of this study but several significant mineralisations are known in upper Rhine valley (France and Germany), in Italy and in Cornwall (England).

Jadar type: The jadar type of Lithium occurrences is regarded as a “non-conventional” lithium occurrence. The occurrence formed in the Lopare basin of NW Serbia and is hosted in 400-500 thick succession comprising clay- silt- and sandstone. The formation of the mineral Jaradarite ($\text{LiNaSiB}_3\text{O}_7(\text{OH})$) is poorly understood. If an economical mineral processing of jadarite is developed by Rio Tinto, the Jadar deposit will be a world-class deposit around 2025.

Lithium bearing bauxites: bauxites can contain variable content of lithium minerals such as Li-bearing clays and Li-manganese oxides. In China Lithium content up to 0.53% Li_2O are found. Some lithium-bearing bauxites are known in Hungary and Greece. EU Potential for this type of deposit should be significant but has never been assessed.

Non economic Lithium mineralisations : Mn(Fe) deposits; These deposits which are normally explored for their Mn and Fe content can contain small amount of the lithium bearing mineral lithiophorite, however in so low content that this deposit type is uneconomic. **Aalenian black shales:** In the Dauphiné region of France lithium levels of around 400 ppm are reported occurring in tension cracks and disseminated in the shale. Lithium enrichment are very local and non-economical.

Cobalt

Pure cobalt does not occur in the nature but cobalt is an element in about 25 minerals. In geological context cobalt behave very similar to nickel and most occurrences of nickel represent occurrences also of cobalt. Very commonly nickel smelters produce a nickel matte which are refined to produce nickel cobber cobalt and PGE metals. It is very rare to find cobalt as the main product of a deposit. The following genetic types of Cobalt occurrences are described in this report:



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STRATEGIC RAW MATERIALS NEEDS

Magmatic Ni-Cu-Co deposits: In these types of deposits cobalt occur in the minerals such as pentlandite ($(\text{Ni,Fe})_9\text{S}_8$) with a typical content from 0.5-3% and in pyrrhothite ($\text{Fe}_{(1-x)}\text{S}$) with a normal content of 0.05-0.2% Co. In general, the nickel content of these deposits determines the cobalt content. Typical deposits of this type in Europe are mafic-ultramafic rock –hosted deposits in Fennoscandia (Finland, Norway and Sweden) with a few rare occurrences elsewhere.

Sediment hosted Cu-Co deposits: These are the most important sources for cobalt with about 64% of the worlds production. Their general setting is in intracratonic sedimentary basins. Typical levels of Cu and Co are in the range 1-5% and 0.01-1-1% respectively. In the Katanga province DRC several large deposits are located with cobalt levels of more than 0.5%. The Kupferschiefer deposits of Poland and Germany are examples of Cu-deposits of this type but they typically contain very low Co contents.

Vein type deposits (5 element vein deposit): These deposits represent hydrothermal deposits where the metals were deposited from hyper saline solutions (>20% NaCl). The typically contain a number of different elements such as silver bismuth, cobalt, nickel and arsenic. A number of the historical mines in central Europe (Czech Republic, Germany, France, Austria, Slovakia, Italy and Spain) are of this type.

Sea floor hydrothermal system (Cu-Zn-Pb VMS deposits): This type deposits are among the worlds most important copper zinc and lead and not uncommonly economical levels and of gold and silver. Cobalt levels are usually >100 ppm and can in some cases reach up to 0.2-0.4%. Cobalt bearing minerals are pyrite, pyrrhothite and Co-pentlandite. The Cu-Zn-Co-Ni deposits of the Outokumpu region in Finland are known for their high Co-contents (0.1-0.25 %) and also produced cobalt in the past.

Lateritic Ni-Co deposits: These deposits are related MgO rich ultramafic rocks of various origins. The primary rock is already enriched in Ni and Co and the weathered laterite contain typically about 1% of Nickel and 0.01-0-0.2% Cobalt. Worldwide they represent an important deposit type for Ni and Co. In Europe there are a number of these occurrences on the Balkan peninsula.

Graphite

The scientific community uses a different approach of classification of carbonaceous material compared to the industry. Somewhat simplified one can say that the academia uses the crystallographic properties of the carbonaceous material for their classification, while the industry uses the grain size and grain properties of the graphite for their classification. The genetic type of graphite using the industrial approach is:

Flake graphite: Flake graphite is graphite formed in metasedimentary rocks of high metamorphic grade. These deposits are characterized by the presence of flakes of individual graphite crystals in variable grain size.



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Amorphous graphite: The term amorphous graphite is misleading, micro crystalline graphite is a more correct description. This type of graphite is formed most commonly from coal deposits altered by contact metamorphism, or from low metamorphic (up to mid greenschist facies) grade organic-rich shales.

Vein or lump graphite: This is a special type of graphite deposit that currently only are mined in Sri Lanka. They are formed by processes that involve the interaction of CO₂, CO, CH₄ and H₂O during metamorphism, subsequent deposition of the carbon from hydrothermal solutions although mined only on Sri Lanka their geological occurrences worldwide are more common.

In Europe the graphite mines in Norway and Ukraine are of flake type and in Austria of amorphous type.

Compared to the occurrences of lithium and cobalt, there is a larger proportion of the graphite occurrences that are unclassified for their genetic type. The reason for this is that geological studies of graphite deposits are much less frequent than studies on other commodities.

1 Introduction

Rechargeable batteries will be the most important cornerstone for the transition to an emission free energy production and storage in the future. The inventors of the Li-ion battery, Michael Stanley Whittingham, John B. Goodenough and Akira Yoshino was given the Nobel prize in chemistry in 2019 for their research and inventions.

Somewhat simplified the schematic construction of a Li-ion battery is shown in Figure 1 below.

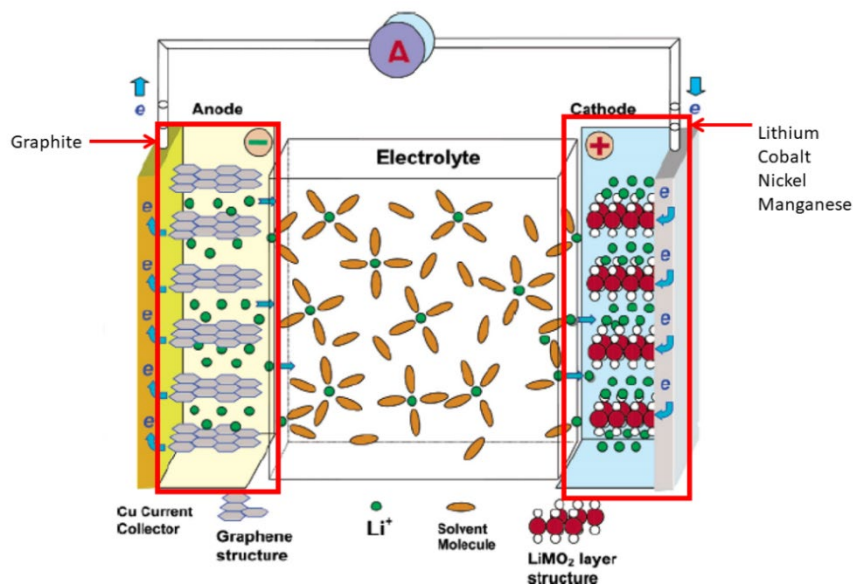


Figure 1 Principle for the construction of the Li-ion battery, where the important materials of the anode and cathode is listed (modified from (Whittingham, 2020)).

We see that lithium, cobalt and graphite are important components in a rechargeable battery, and thus also in every finished product where batteries are used. In this report we aim to give the reader an introduction to the complexities in the formation and enrichment of lithium, (Li) cobalt (Co) and graphite, we will emphasize the geological settings we have in Europe.

In most cases where minerals are mined and processed they represent, usually a cheap part of the value chain from mining to manufacturing a composite product such as a battery.

This is the second deliverable (D5.2) of the work package 5 (WP5) of the FRAME project and a direct continuation of the first D5.1. The aim of D5.1 was to give overview of the metallogenetic provinces and occurrences of Li, Co and graphite in Europe, therefore this topic will only when necessary be discussed in this report.

There is an integrated co-operation between the different work packages of the FRAME project where for instance WP 5 collects, systemize and prepare occurrences information on lithium, cobalt and graphite in Europe for WP 3 and the data from WP5 are already an integrated part of the deliverables D.3.2 and D3.3. (Sadeghi et al., 2020a, 2020b).

The energy critical elements (ECE) lithium cobalt and graphite have an each a very different and complex mode of formation and occur in many different deposit groups and geological settings.

The aim of this deliverable is to give a review of this complexity and to give descriptions of the various deposit groups and their processes of formation. Due to the difference and complexity

between lithium cobalt and graphite the sub chapters covering each of these will naturally be very different. In addition, comes the fact that no ECE occur in nature as a finished saleable product, but are usually a minor constituent in different minerals that must be separated and concentrated to a mid-product before saleable product can be processed and purified. This relationship is well illustrated with the so called “wheel of metal companionship” (Nassar et al., 2015) (Figure 2).

In this review, we have tried to make our descriptions so simple that a detailed geological knowledge in ore-, metamorphic- or igneous- petrology should not be necessary. Only where it is needed, we will go into detail. We will follow approach of standard textbooks of economical geology. This deliverable will be a kind of support material for D5.1, D3.2, D3.3 and the forthcoming D5.3.

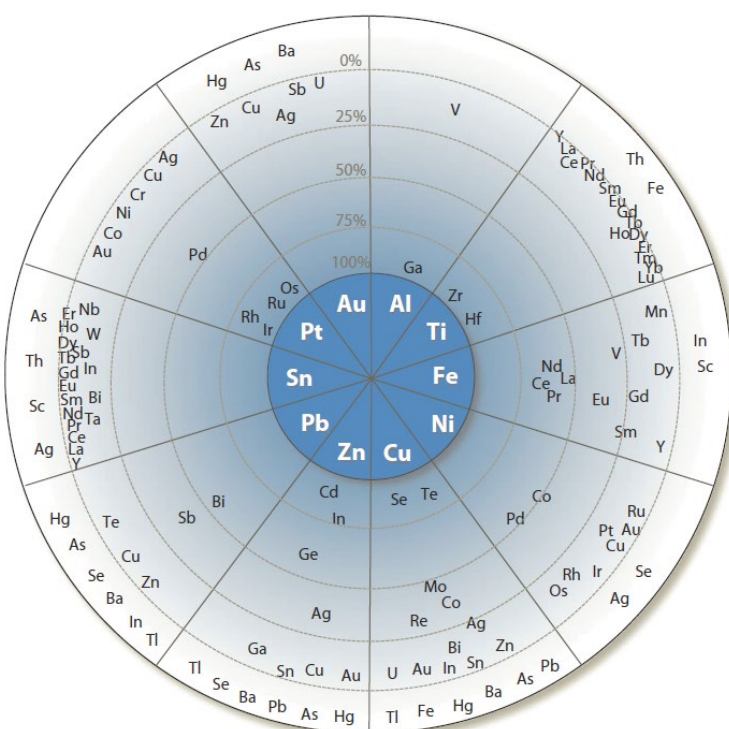


Figure 2 The wheel of metal companionship.

The wheel of metal companionship shows the principal host metals from the inner circle. Companion elements appear in the outer circle at distances proportional to the percentage of their primary production (from 100 to 0%) that originates with the host metal indicated. The companion elements in the white region of the outer circle are elements for which the percentage of their production that originates with the host metal indicated has not been determined. From (Nassar et al., 2015).

2 Materials and methods

2.1 Data material and source

The work package 5 (WP5) collected information related to the occurrences from its project partners and in addition data from a large number of MREG members. Details regarding the type of data, code list and data vocabulary is listed in Appendix 1. This information organised in excel and used for the constructions of maps and tables. Early in the start of the GeoEra program there was an urgent interest from the DG Grow for data on Li-Cobalt and graphite occurrences in Europe as part of the battery action plan (Mancini et al., 2020). Due to this urgency the bulk of the data was collected as early as possible and before the standards of the GeoEra information platform project (GiP-P) was fully established. This has resulted in some difficulties in the integration of WP5 data in GiP-P and the EGDI (European Geodata Information Platform). However, it must be emphasized that WP 5 has been able to collect the necessary data full fill all milestones according to plans and deliver to stakeholders beyond what was initially planned. For instance, WP5 delivered maps for display In the EU commission booth at the PDAC conference in Toronto in 2019 and 2020.



3 Lithium

3.1 Properties of Lithium

Lithium is the third element of the periodic table because it contains 3 protons ($Z = 3$), which defines its place in the Mendeleïev periodic table of the elements. It is a very light alkaline metallic element with a density of 0.53, which is half as dense as pure water. The average ionic radius of lithium is 0.76 Å. It is very similar to the ionic radius of magnesium (0.72 Å), which explains the frequent substitution of magnesium by lithium in minerals. In pure form, it is a silvery-coloured, soft, breakable metal that melts at only 180.5 °C. In metallic form, it oxidizes in air to form lithium oxide Li_2O . Because of its very high reactivity, especially with water or air, it does not exist in its native state. It has a high boiling point of 1342 °C. It is the element with the highest specific heat, 3582 J / (Kg·K). Lithium has 3 electrons, 2 on the first electron shell and a single electron on the second shell. The first layer of electrons has the effect of reducing the attraction of the protons on the electron of the second (external) layer which explains the low electronegativity of lithium, 0.98 on the Pauling scale, one of the lowest among all the elements. Then, lithium atom can very easily lose its electron in favor of a more electronegative element to form the Li^+ cation. Lithium exists as two natural and stable isotopes, 92.5% as ^7Li and only 7.5% as ^6Li . Lithium 7 (^7Li) is one of the few nuclides to have been formed during the Big Bang, while very little ^6Li was generated during this event. The large mass difference (~ 16%) between ^6Li and ^7Li can allow significant isotopic fractionation and this property is used to understand many deep geological or surface processes.

3.2 Lithium minerals

A minimum of 120 mineral species containing lithium are listed in the database of the International Mineralogical Association (IMA, <http://rruff.info/ima/>). This is a minimum because several mineral species containing small amounts of lithium are not counted. These 120 species are 73% silicates, 19% phosphates and 8% oxides, hydroxides, arsenates, chlorides or fluorides (Grew, 2020; Grew et al., 2019). Of these species, ~12 species are the most common (Table 1), i.e. with more than 50 known occurrences worldwide (Grew, 2020). Conversely, jadarite $\text{LiNaSiB}_3\text{O}_7(\text{OH})$, a mineral of the zeolite family, is only known in the Jadar mineralization in Serbia (Stanley et al., 2007), but could represent an important European deposit in the coming years. The families of minerals containing the most lithium are phosphates, inosilicates and neosilicates followed by phyllosilicates. Lithium mineralization will therefore depend on the lithium mineral species present in the rock and their relative proportions in it. Spodumene is the most abundant of the lithium-rich minerals (8% by weight), which is in part the reason why lithium extraction processes have been developed for this mineral since a long time.

Li₂O wt. %	Mineral	Formula	Group	Molecular weight (gm)
10.20	Montebrasite	$\text{LiAl}(\text{PO}_4)(\text{OH},\text{F})$	Phosphate	146.4
9.54	Lithiophilite	LiMnPO_4	Phosphate	156.85
9.47	Triphylite	$\text{LiFe}^{2+}\text{PO}_4$	Phosphate	157.76
8.03	Spodumene	$\text{LiAlSi}_2\text{O}_6$	Inosilicate	186.09

7.41	Amblygonite	$(\text{Li,Na})\text{Al}(\text{PO}_4)(\text{F,OH})$	Phosphate	151.41
7.28	Jadarite	$\text{LiNaB}_3\text{SiO}_7(\text{OH})$	Nesosilicate	221.63
6.46	Polyolithionite (Lepidolite)	$\text{KLi}_2\text{AlSi}_4\text{O}_{10}(\text{F,OH})_2$	Phyllosilicate	393.12
5.62	Trilithionite (Lepidolite)	$\text{KLi}_{1.5}\text{Al}_{1.5}\text{AlSi}_3\text{O}_{10}\text{F}_2$	Phyllosilicate	399.21
4.76	Borocookeite	$\text{Li}_{(1+3x)}\text{Al}_{(4-x)}(\text{BSi}_3)\text{O}_{10}(\text{OH,F})_8$ [x=0-0.33]	Phyllosilicate	502.73
4.50	Petalite	$\text{LiAlSi}_4\text{O}_{10}$	Phyllosilicate	305.15
4.07	Elbaite	$\text{Na}(\text{Li,Al})_3\text{Al}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_4$	Cyclosilicate	916.68
3.42	Zinnwaldite	$\text{KLiFe}^{2+}\text{Al}(\text{AlSi}_3)\text{O}_{10}(\text{F,OH})_2$	Phyllosilicate	437.1
3.16	Lithiophorite	$(\text{Al,Li})\text{Mn}^{4+}\text{O}_2(\text{OH})_2$	Hydroxyde	141.92
2.86	Cookeite	$\text{LiAl}_4(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$	Phyllosilicate	522.16
1.16	Hectorite	$\text{Na}_{0.3}(\text{Mg,Li})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	Phyllosilicate	383.25

Table 1 : Most common Li-bearing minerals. Data source: IMA

3.3 Behaviour and distribution of lithium in geological processes

3.3.1 Distribution of lithium in rocks

Compared to other alkali metals such as sodium and potassium, which are major constituents of the upper continental crust, lithium is much less abundant with an average abundance of only 0.002% (Taylor & McLennan, 1985). The average concentration of Lithium in the upper continental crust is around 35 ± 11 ppm (Teng et al., 2004), three times greater than in the oceanic crust and basalts (Table 2). The granites would have an average concentration of 30 ppm but this average masks a very great variability. Peraluminous granites are generally much richer in lithium. As an example, Variscan peraluminous granites from English Cornwall have an average content of between 108 and 445 ppm (Simons et al., 2017) variably depending of the granite generation and excluding rare metal granites. Marine sediments rich in clay are relatively Li-rich, on average in the range of 60 to 80 ppm, but again this average masks a great disparity. As a first approximation, detrital aluminous sediments seem to have an average lithium content above the average for the upper continental crust, as well as crustal granites that derive from the partial melting of sediments (Table 2).

Lithology	Lithium concentration (ppm)
Mantle	1.5 ^b
Oceanic crust (MORB)	9 ^a , 10 ^b
Lower continental crust	13 ^b
Upper continental crust	20 ^a ; 35 ± 11 ^b
Granites	30 ^a
Micaschists	34 ^a
Hemipelagic clays	79 ^a ; 57 ^c
Deep marine carbonates	5 ^c
Clays	45 ^a ; 42 to 77 ^b
Marine clays	66 ^a ; 28 to 109 ^b
Continental clay (rivers)	30 ^a
Loess	35 ^a ; 29 ± 16 ^b
Soils	33 ^a
Secondary bauxites	47 to 613 ^d

Table 2: Average lithium concentration for various terrestrial reservoirs, igneous and sedimentary rocks and soils. Data from: a) (Li, 2000); b) (Teng et al., 2004); c) (Taylor & McLennan, 2008); d) (Ling et al., 2018).

3.3.2 Behaviour of lithium in geological processes

3.3.2.1 Metamorphic processes

Due to the similar ionic radius between Li⁺ (76 pm) and Mg²⁺ (72 pm), lithium, in six-fold coordination in the phyllosilicates (Wenger & Armbruster, 1991), substitutes for magnesium in the octahedral sites as well as in the interfoliar position to balance charges in clays. On the earth's surface, lithium is thus mainly carried by clays, produced in particular by supergene weathering. The lithium concentration in metapelites is thus greater when they originate from continental domains with strong supergene alteration (Qiu, 2011). From diagenesis to the greenschist facies, lithium remains with magnesium successively in smectites, illites and then chlorites as the temperature increase. This would have only a negligible effect on the lithium concentration of the metapelites near the greenschist facies (~ 300 °C). Conversely, the metamorphic dehydration of the greenschist facies to the granulite facies can lead to a significant loss of lithium, but this loss is not systematic. Indeed, one of the key factors in the preservation of lithium in metapelites during metamorphism is the stability of hydrated magnesium aluminosilicates: chlorite, biotite and staurolite. In particular, staurolite is by far the richest mineral in lithium compared to other minerals in metapelites (Dutrow et al., 1986). Thus, following the pressure-temperature path and mineralogical transformations, lithium is increasingly mobilized by the fluid (Chan et al., 1994; Chan & Kastner, 2000) above the temperature of transformation of smectite into illite. If lithium mineralogical carriers are destroyed, the amount of lithium lost by the metasediment in contact with the fluid will depend on: i) the temperature at which the loss of fluids takes place (Chan & Kastner, 2000; Millot & Négrel, 2007; Scholz et al., 2010; Scholz et al., 2009; Vigier et al., 2008) but also of ii) the nature of newly formed minerals and their ability to integrate lithium into their structure. Thus, a sedimentary formation can lose 20 to 50% of its initial lithium content during metamorphic dehydration reactions between 250 and 650°C (Marschall et al., 2007; Qiu et al., 2011; Teng et al., 2007; Zack et al., 2003) and even beyond in temperature, some examples suggest that the

transition from the amphibolite facies to the granulite facies can lead to the loss of 90% of the lithium initially contained in the metapelites (Qiu et al., 2011).

3.3.2.2 Magmatic processes

Following the emplacement of felsic intrusion and during its cooling, the crystallization of anhydrous minerals such as potassium feldspar (~40% vol.), Quartz (~30% vol.) and plagioclases (~20% vol.) led to an increase of the relative concentration of incompatible elements (H₂O, Li, P, LILE, HFSE) in residual magma. This is because the mineral / granitic magma partition coefficient for lithium is very much in favour of magma with partition coefficients between 0.05 and 0.1 for the anhydrous minerals that represent around 90% of the crystals. However, some of these elements will be integrated into hydrated minerals ($\pm$ muscovite $\pm$ biotite $\pm$ amphibole $\pm$ apatite) and oxides. In fact, some of the lithium in particular is integrated into the remaining ~ 10% of white and black micas in which the lithium is partially compatible (Icenhower & London, 1995). Successive fractional crystallization phenomena within granodioritic to granite intrusive complexes should lead to the generation of residual magmas enriched in dissolved water and volatile elements (Černý et al., 2005).

3.3.2.3 Hydrothermal processes

In hydrothermal systems, the partitioning of lithium between fluids and rocks during fluid-rock interaction depends on several parameters. The main parameters are the fluid-rock interaction temperature, the type of fluids (salt content, pH, etc.), the lithium content of the host rocks, the mineralogical carriers of lithium and the structural position of lithium (exchangeable versus not exchangeable), particle size and porosity-permeability (Romer et al., 2014). From these parameters, the fluid-rock interaction temperature is one of the most important. This is illustrated, first, with the overall increase in lithium concentration in different types of fluids with temperature (Fouillac & Michard, 1981) and, second, with the existence of geothermometers based on the Na / Li ratio (Sanjuan et al., 2014) and references included). During weathering of lithium-bearing rocks by fluids, there is a competition between the dissolution rate of primary minerals and the formation rate of secondary minerals (Pogge von Strandmann et al., 2020). If the primary minerals are dissolved without formation of secondary minerals, mainly clays, the lithium content of the fluids will be significant and the isotopic signature of lithium will retain the signature of the primary rock. Conversely, if there is a significant formation of secondary minerals, these minerals will sequester a large part of the lithium and will induce a change in the lithium isotopic signature of the fluid. The lithium content of the fluids will therefore depend of the lithium concentration of the primary rocks (which refers to the mineralogical carriers of lithium), will depend of the chemical composition of the fluids present and will depend of their temperature. Lithium can be integrated in smectites, smectite-chlorite interlayer, in illites and in chlorites eg. (Milot et al., 2010) and references included. Between 200 and 300°C, lithium is partitioned between the fluid and the newly formed clay minerals (Pogge von Strandmann et al., 2016). In experiments on crystallization of lithiniferous smectites, whether dioctahedral (Li-montmorillonites) or trioctahedral (hectorites) smectites, the amount of lithium integrated in the smectites increases between 25 and 250°C (Calvet & Prost, 1971; Vigier et al., 2008). For example, laboratory experiments show that the lithium hectorite concentration drops from 120 to 3400 ppm between 25 and 250°C (Vigier et al., 2008). Conversely, in high temperature geothermal systems, above 300°C, the formation of clay minerals is inhibited and lithium is partitioned in the geothermal fluid (Pogge von Strandmann et al., 2016) which therefore sees an increase of its lithium content.

3.4 Model of formation of lithium mineralisation

3.4.1 Lithium mineralisation associated with deep processes

3.4.1.1 Lithium-Cesium-Tantalum Pegmatites

According to (London, 2008), the definition of a pegmatite is the following: *an essentially igneous rock, commonly of granitic composition, that is distinguished from other igneous rocks by its extremely coarse but variable grain-size, or by an abundance of crystals with skeletal, graphic or other strongly directional growth-habits. Pegmatites occur as sharply bounded homogeneous to zoned bodies within igneous or metamorphic host-rocks.* To this definition, it should be added that pegmatites are bodies with a volume of a few cm³ to less than 1 km³. Moreover, a pegmatite is never isolated but in groups of several bodies of variable geochemistry, up to several thousand individuals bodies (Černý et al., 2005), which are distributed as clusters of pegmatites (Deveaud et al., 2013). The few studies that have focused on the emplacement of pegmatites (Demartis et al., 2011; Deveaud et al., 2013; Silva et al., 2018) demonstrate an important structural control of their emplacement, emphasizing the role of faults (drain) and the maximum compressive stress (tension gashes) as well as the pressure of the fluids associated with the crystallization of pegmatites (Brisbin, 1986).

There is a great chemical and mineralogical variety in pegmatites. The most widely used classification of pegmatites is that of (Černý & Ercit, 2005) which classifies them in two main families (Table 3), Lithium-Cesium-Tantalum (LCT) and Niobium-Yttrium-Fluor (NYF). Each family is then subdivided into class, subclass, type and subtype. Economic lithium pegmatites (> 0.5% Li₂O, for both ceramic and battery industries) correspond only to certain types and subtypes of the LCT family pegmatites. In other types and subtypes, lithiniferous minerals may be present in the late stages of crystallization but the volume of lithiniferous minerals is very small. These include lepidolite and lithium phosphates (lithiophilite-triophyllite) found in the albitic portions of pegmatites of the beryl-columbite-phosphate subtype.

The pegmatites of the LCT family are pegmatites of crustal origin, similar in composition to S-type granites which are related to the partial melting of aluminous metasediments (Chappell & White, 1992). They are therefore mainly encountered, as well as crustal granites, in continental collision settings where the partial melting of metasedimentary sources are widespread. The LCT pegmatites are peraluminous rocks, with a mineralogy consisting mainly of quartz, potassium feldspar, albite, ± biotite, ± muscovite, ± garnet, ± cordierite, ± sillimanite / andalusite, ± tourmaline. Enrichments in lithium, cesium and tantalum - even relative - are one of the most marked characteristics of LCT pegmatites (Černý et al., 2012). In LCT pegmatites, the main lithium-carriers are spodumene, petalite, elbaite, the lepidolite series and phosphates of the amblygonite-montebrazite and lithiophilite-triophyllite series. Cesium is generally present in micas and beryl, more rarely in the most geochemically evolved pegmatites in the form of pollucite (CsAlSi₂O₆) (Černý et al., 2005; London, 2008). Tantalum is generally contained in colombo-tantalite oxides with niobium as well as in cassiterite (Artemieva et al., 2006; Tindle & Breaks, 1998) but also in tantalum oxides at the end of crystallization of the most advanced pegmatites. Apart from lithium, cesium and tantalum, these LCT pegmatites are remarkable for their content in various flowing elements such as phosphorus, boron or fluorine.

At world scale, the number of economical lithium pegmatites remains extremely low compared to the total of pegmatites and there are two main models of genesis of LCT pegmatites, the

model of granitic genesis and the model of anatectic genesis e.g., (Černý et al., 2005; London, 2008).

Class	Sub-class	Type	Sub-type	Family
Abyssal	HREE			NYF
	LREE			
	U			NYF
	BBe			LCT
Muscovite				
Muscovite-rare element	REE			NYF
	Li			LCT
Rare element	REE	Allanite-monazite		NYF
		Euxenite		NYF
		Gadolinite		NYF
	Li	beryl	Beryl-columbite	LCT
			Beryl-columbite-phosphate	LCT
		complex	spodumene	LCT
			petalite	LCT
			lepidolite	LCT
			elbaite	LCT
			amblygonite	LCT
		Albite-spodumene		LCT
		Albite		LCT
Miarolitic	REE	Topaze-beryl		NYF
		Gadolinite-fergusonite		NYF
	Li	Beryl-topaze		LCT
		spodumene		LCT
		petalite		LCT
		lepidolite		LCT

Table 3: Pegmatite classification according to (Černý & Ercit, 2005). Economic lithium-pegmatites are in bold

3.4.1.1.1 Model of granite source

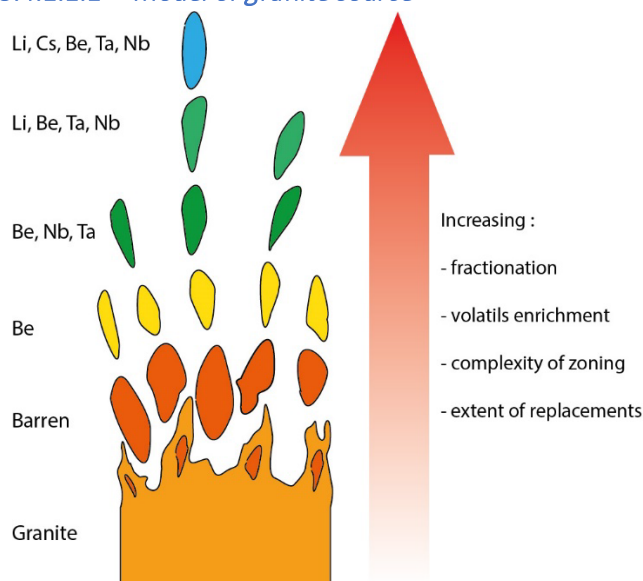


Figure 3: Chemical evolution through a lithium-rich pegmatite group with distance from the granitic source. Modified from London (2008)

During the crystallisation of a felsic intrusion, the residual magma is progressively enriched in incompatible elements. This residual magma is concentrated by buoyancy at the top and edge of the so-called “parent” granites to form pegmatites. Pegmatites therefore represent the last fraction of magmatic liquid resulting from a very important crystallization process, the crystallization of the entire intrusion. However, there is no correlation between the granite volume and the pegmatite volume because the granite intrusions associated with rare-element pegmatite fields vary greatly in volume, from small

intrusions to batholiths (Černý et al., 2005). Since the pioneer work of (Jahns, 1982; Jahns, 1955), the evolutions of numerous ratios of major elements and trace elements (Rb/Sr, Rb/Ba, Na/K, Zr/Hf, Nb/Ta, LREE/HREE, Li/Cs, etc) and the geochemical similarities between the different facies of granites and the spatially associated pegmatites are considered as a demonstration of the process of filiation and fractionation. The rise of pegmatitic magmas must itself be associated with fractionation phenomena as the magmas move away from their parent intrusion (Figure 3). These ascension and fractionation processes during the ascent of pegmatitic magmas are not yet well understood (London, 2008). This author suggests the existence of a vertical chemical zonation of the magma in the intrusion and an extraction at various levels of the pluton by filter-press mechanisms which would expel the pegmatitic magmas in the host. Other mechanisms are proposed, such as crystal-magma segregation by turbulent flow in intrusion roof dykes eg (Yamato et al., 2015). The zonation observed in the pegmatitic fields around the plutons, with barren pegmatites close to the granites and more and more enriched ones far from the parent granite, would thus be linked to these phenomena of ascent and fractionation during the rise of pegmatitic magmas.

3.4.1.1.2 Partial melting model

This model, proposed by several authors, assumes that pegmatites originate from crustal rocks undergoing partial melting e.g., (Norton, 1973). To form liquids of adequate composition, the partial melting percentage must be very low so that the magmatic liquids produced are as rich as possible in incompatible elements. Moreover, a low partial melting rate implies the production of a low volume of magma, which is one of the characteristics of pegmatites (10^{-6} to 10^{-3} Km³), volumetrically from 3 to 10 orders of magnitude lower than for granites (1 to 10^4 Km³, (Jellinek & DePaolo, 2003)). The sources must correspond to crustal sediments, in particular enriched metapelites (Gourcerol et al., 2019) in which incompatible elements have not been lost during prograde metamorphism (Figure 4). The minerals carrying lithium can be muscovite, biotite, staurolite. In addition, the carrier phases must be able to be mobilized in the partial melting process. Due to the low melting rate, anatectic liquids are not connected. Thus, very specific conditions must allow the extraction of these drops in a matrix

which can be likened to extracting drops of magma from a solid sponge. Several hypotheses are possible:

- The matrix is strongly anisotropic (metamorphic foliation), which favours the connectivity of the magma drops produced, a bed by bed fusion and the migration of the fusion products upwards by buoyancy.
- The matrix undergoes a strong compression (pure shear) and/or a shearing strain (simple shear) allowing the collection of the partial fusion products.
- The permeability is high (dynamic permeability) and the magma / migmatite viscosity contrast is very strong which allows the extraction and the ascent in the form of a solitary wave (Figure 8) of pegmatitic magma (Deveaud, 2015; Deveaud et al., 2015).

These hypotheses put in parallel phenomena which have kinematics which differ by several orders of magnitude between the speed of a magma (several cm to meters/year) and the speed of deformation (0.3 cm/year maximum). But the average strain rate results from a sum of instantaneous strains (e.g., an earthquake) where the speed is very fast but for a small volume. It is therefore the instantaneous speed that must be considered in a similar way to the difference between the static and dynamic permeability of a rock. The residence time of the liquid produced in the source is also a parameter. These liquids must also undergo fractionation processes during their ascent to reach the observed concentrations (London, 2005). The soliton-type mechanism, already proposed for magmas e.g., (Coumou et al., 2006), as well as liquid-crystal separation e.g., (Yamato et al., 2015) could be efficient fractionation mechanisms during the ascent of pegmatitic magmas.

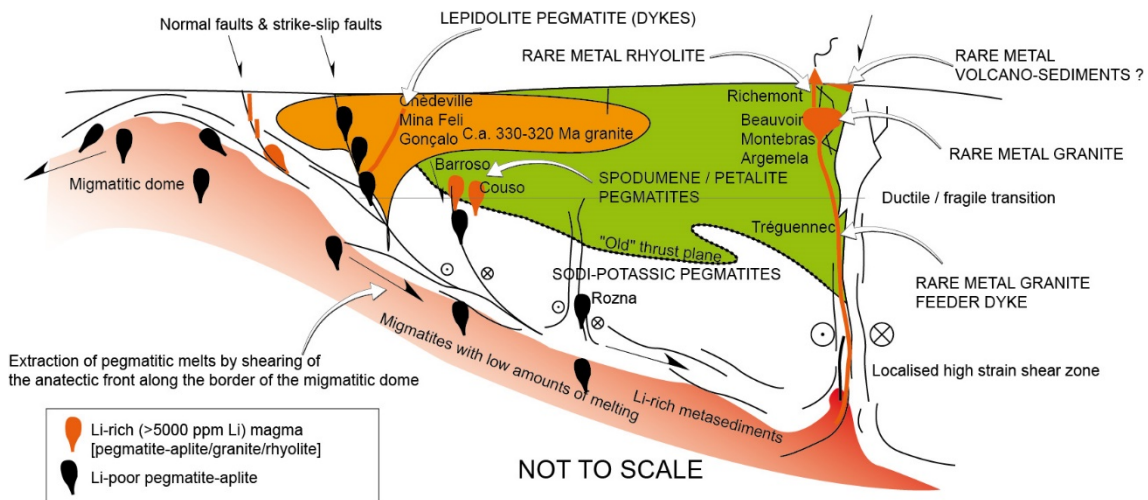


Figure 4: anatectic model for the generation of pegmatites (barren and Li-rich) and rare-metal granites. Some European mineralisation are given. Modified from Gourcerol et al (2019).

3.4.1.2 Rare metal granites

Rare metal granites, as defined by (Černý et al., 2005) and (Linnen & Cuney, 2005), are albite-rich quartz-poor granites, peralkaline to peraluminous in composition, showing a clear magmatic enrichment of various metals, with extremely low Zr/Hf and Nb/Ta ratios (respectively <18 and <5, (Ballouard et al., 2016)) with an element spectrum related to their geochemistry. This metal enrichment results in mineralization disseminated throughout the mass of the granite (Černý et al., 2005; Cuney et al., 1992; Linnen & Cuney, 2005). These granites are found mainly

in late-orogenic contexts but also in subduction contexts (in the form of porphyries) or even in anorogenic context.

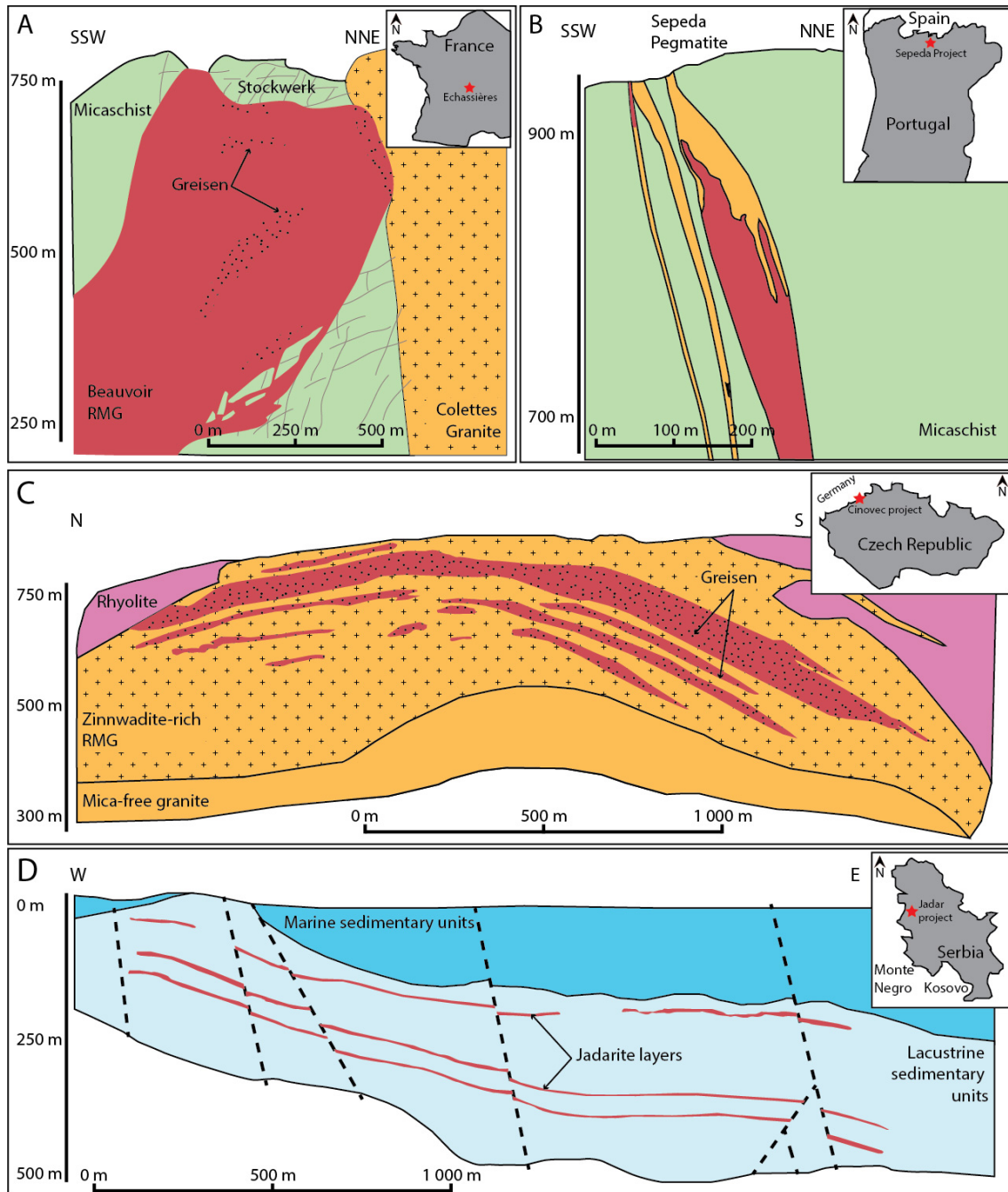


Figure 5: Cross sections of various lithium deposits. Lithium-bearing units are identified in red in each section. A) Beauvoir RMG (France) and related stockwork; B) Sepeda pegmatite in Portugal; orange area represents barren pegmatite. C) Cinovec deposit in Czech Republic; D) Jadar Basin in Serbia and location of the jadarite layers; modified from Gourcerol et al (2019) and references enclosed.

They are emplaced close to the paleosurface in the form of isolated intrusive bodies, of very small size, less than or equal to 1 km³ (Beauvoir, France; (Cuney et al., 1992), Figure 5A), of microgranite dykes (Tréguennec, France;(Lulzac & Apolinarski, 1986)) of rhyolite (Richemont, France;(Rimbault & Burnol, 1998) or volcanic rocks such as Spor Mountain (USA) which is the world's largest deposit of beryllium (Dailey et al., 2018) and references included). Rare metal granites are divided into three groups(Černý et al., 2005; Linnen & Cuney, 2005): i) rare metal

peralkaline granites; ii) metaluminous to peraluminous granites poor in phosphorus and iii) peraluminous granites rich in phosphorus. Only the latter represent lithium deposits, mainly for the glass and ceramics industry. The peraluminous granites rich in phosphorus and albite show strong enrichments in tantalum, tin, fluorine and lithium and are formed in contexts of continental collision. In these types of granites, the average lithium concentrations vary greatly between 0.5 and 1% Li₂O. These concentrations are carried by various minerals such as phosphates (amblygonite-montebrazite) and phyllosilicates (polyolithionite-trillithionite, Li-muscovite, more rarely zinwaldite). Representative examples are the intrusions of the northern Massif Central such as Beauvoir (Allier) and Montebraz (Creuse) and their volcanic equivalent, the rhyolite of Richemont (Haute-Vienne), or the dykes of Tréguenec (Finistère) or the intrusion of Argemela in Portugal. The geochemistry and enrichments of these granites are similar to that of lithium-rich LCT pegmatites, which are also rich in phosphorus.

The preferred hypothesis for the genesis of these rare metal granites rich in phosphorus is that of a partial melting of metasediments (Černý et al., 2005) (Figure 4). Nevertheless, these rare-metal granites could also represent the last injection, and the most fractionated, within vertically differentiated plutons (Cuney et al., 1992; Kovalenko et al., 1970; Yin et al., 1995). We therefore find a strong similarity between these rare metal granites rich in phosphorus and the LCT pegmatites. The metallogenic models are therefore partly similar and not repeated here. An important point seems to be the spatial link between rare metal granites and large ductile shear zones of a priori crustal scale (Gourcerol et al., 2019).

The main differences between rich and phosphorus rare metal granites and LCT pegmatites are the difference in volume (granite >> pegmatite), the difference in the number of intrusions (granites with rare metals in isolated intrusions or of a few rare individuals to compare to pegmatite fields of several hundred individuals), the difference in the structural level of placement because the rare metal granites are not observed within the pegmatite fields, and generally show a placement close to the surface (volcanic or subvolcanic facies). These 3 points converge to suggest that the processes of generation of magmas for granites and pegmatites are similar but that the extraction and the ascent of these magmas could be favoured by the presence of large structure of unhooking ductile faults (Gourcerol et al., 2019).

3.4.1.3 Greisens

Greisens correspond to some parts of granite intrusion transformed by hot hydrothermal fluids into an assemblage mainly composed of muscovite and quartz (Černý et al., 2005) (Figure 5C). Greisens are porous rocks and in these pores can be found apatites, cassiterite and sulphides. Greisens are located at the roofs of granite intrusions as well as along faults intersecting the granites. The existence of granite apex where hydrothermal fluids focus (Launay, 2018; Launay et al., 2019) can lead to total greisenification of the apex with greisens thickness that can exceed 100 m. The formation of greisens is linked to the circulation of acidic and hot magmatic fluids resulting from the end of crystallization of the granitic magma. These fluids hydrolyze feldspars and biotites and remove solubilized elements, which leads to the formation of porosity in the greisen despite the development of hydrothermal muscovite. It has been demonstrated by Launay (2018) that greisens are active alterations which, by creating porosity, greatly improve hydrothermal circulations leading to the formation of mineralization.

Greisens developed in peraluminous crustal granites classically associated with Sn-W deposits are greisens sometimes mineralized in tin (cassiterite) but do not appear to lead to the formation of lithium enrichment. For example, the world-class W-Sn- (Cu) deposit of

Panasqueira (Portugal) contains greisens averaging around 732 ppm Li_2O (Bussink, 1984). Conversely, the greisens developed on the rare metal peraluminous granites poor in phosphorus, can be mineralized in lithium while the host granite is poorly mineralized. For example, the rare metal granite from Cinovec (border Germany-Czech Republic) contains an indicated resource of 372.4 Mt of mineralized greisens grading 0.4% Li_2O mainly in the form of zinnwaldite. Other co-products are associated with lithium in these greisens, including tin and tungsten and other small metals (In, Sc, etc.), as appropriate. These greisens are to be prospected on the roofs of granites with poor peraluminous rare metals and phosphorus and along the zones of faults or hydrothermal veins of high temperature intersecting them.

3.4.1.4 Lithium-phosphate quartz vein

At the end of the crystallization of rare metal granites, high temperature hydrothermal fluids, mainly rich in silica, phosphorus, lithium and fluorine are sometimes produced (Roda-Robles et al., 2016). When these fluids are trapped, they form veins or veins of lithium quartz phosphates. These are generally phosphates of the amblygonite-montebasite series of the general formula $(\text{Li}_{1-x}\text{Na}_x)\text{Al}(\text{PO}_4)(\text{OH},\text{F})$. These veins are mainly observed within or near rare metal granites (Roda-Robles et al., 2016). The best-known example of a quartz-amblygonite vein system is represented by the rare metal granite of Argemela and the quartz-amblygonite mine of Argemela in Portugal (Michaud et al., 2020). These hydrothermal fluids can also diffuse within the formations surrounding the rare metal granites and form large diffusion halos. These halos can be highlighted by geochemistry campaigns in stream sediments and/or in soil geochemistry. The geochemical halo in micaschist that host the rare-metal granite of Beauvoir (France) is a good example (Aubert, 1969).

3.4.2 Lithium mineralisation associated with surficial processes.

3.4.2.1 Stratiform sedimentary-hydrothermal lithium mineralisation

Stratiform sedimentary-hydrothermal lithium mineralisation are witnesses of environments or paleoenvironments that share a large number of common characteristics. Indeed, the formation of stratiform lithium mineralisation requires the trapping of a lithium flux on a fixed place over a certain period of time. The trap is typically represented by a physical depression that could be a closed, semi-closed or unclosed continental sedimentary basin as well as a volcanic caldeira, preferentially localised in a sedimentary basin. The lithium flux is provided by surficial water and groundwater that originate from volcanic and/or basement rocks regionally surrounding the trap. A part of the lithium flux may also be provided by a volcano-sedimentary detrital fraction deposited in the sedimentary sequence. Magmatic brines could also contribute to the lithium stock (Castor & Henry, 2020). The trapping of lithium-bearing waters is variably realised by the competition between the evaporation rate and the aperture degree of the basin (or the trap). The most significant lithium mineralisation is then encountered under arid climate in endorheic basin surrounded by rocks whose lithium is leachable.

Depending on the climate and the detrital supply, the sedimentary trap infill will alternate or vary from evaporites sequences to detrital sequence (clays, sand, etc). Stratiform lithium mineralisation are mainly represented by Li-bearing clays, Li-bearing salts (evaporites) and associated brines.

3.4.2.1.1 Clay-type

Lithium-bearing clays correspond to several clay species in which the lithium could be integrated in the clay structure, exchangeable being in the interfoliar position or adsorbed as

ion at the clay surface. Depending on the lithologies and the alteration conditions, various types of Li-bearing could be formed including true clay: trioctahedral smectite (e.g., Hectorite), dioctahedral smectite (e.g., Li-Montmorillonite), interstratified chlorite-smectite (e.g., Li-Tosudite) and chlorite (e.g., cookeite). The lithium-clay deposits of the 40 x 25 km Miocene McDermitt caldera (Oregon, USA) are a good example (Castor & Henry, 2020). The lithium mineralisation is hosted by a ca 200m-thick sedimentary sequence mostly composed of altered tuffaceous sediments originally mainly composed of Li-rich rhyolitic volcanic glasses (Benson et al., 2017). This sedimentary sequence has been altered by a closed hydrologic system within the Caldeira, with a fluid circulation driven by the volcanic heat at depth. The mineralisation, that contains 2000 to 3000 ppm Li, occurs as layers of hectorite (Li-smectite) that evolves to illitic clays at depth due to the transformation from smectite to illite with increasing temperature. Interestingly, the lithium content of some clays layers is under evaluation by exploration companies.

3.4.2.1.2 Brine-type

Lithium brine deposits are localised in recent continental basins containing lacustrine evaporites generated by high rates of evaporation relative to precipitation (Kesler et al., 2012) (Figure 6). According to (Bowell et al., 2020), lithium brines are typically defined as hypersaline, with salinity ranging between 1.7 and 24 times that of seawater. Lithium brines tend to be characterized by concentrations of dissolved ions that are near saturation for many salts, particularly halite in the mature salars. Brines are composed of several ions including sodium, chlorine, potassium, boron, sulfate and lithium. Nevertheless, the lithium enrichment of continental brines is not systematic, highlighting the fact that lithium needs to be sourced from some suitable geological sources (volcanic glasses, favourable basement rocks, etc). Lithium brines are pumped to an area where salts can be concentrated by evaporation or be extracted by chemical separation.

Non-geothermal brine deposits are encountered within various types of geological environments defined by two end-members (Figure 6), mature chemically supported salars and immature clastic-dominated salars (Houston et al., 2011). Mature salars are observed in more drier regions (e.g., W Puna, Argentina; Sonora) whereas immature salars occur in wetter regions and/or in wetter climatic periods (NE Puna, Tibet) (Bowell et al., 2020; Houston et al., 2011). Mature salars are dominated by a massive halite core, with minor beds and lenses of clastic (silt/clay, sand) sediments (Figure 6). The halite core is made of a thin upper porous halite layer and a lower thick sequence of massive halite. At depth, pore spaces are completely filled by the diagenetic cementation, leading to a thick (>60–70 m) sequences of massive halite (e.g., Warren, 2010). Immature salars are dominated by detrital sediments such as clay, silt, and sand with some interbedded evaporites (halite and gypsum). In these salars, generally the brines do not reach the halite saturation due to wetter conditions. The brines volumes are generally high due to the high porosity of the detrital sedimentary layers and several brines aquifers could be encountered at depth.

The Clayton Valley (Nevada, USA) is an example of lithium-brine mineralisation hosted by a clastic-dominated basin. The Clayton Valley is located in the Basin and Range Province of the Western United States and is characterized by an arid climate. It corresponds to a semi-closed basin, bordered by high mountains including a metamorphic core complex and normal fault system. The sediments deposited in the basin are primarily silt, sand and gravel interbedded with illite, smectite and kaolinite clays (Munk et al., 2016) and references therein). The basin is also filled by Miocene to Pliocene silicic tuffs and rhyolites and tuffaceous lacustrine facies which

contain significant lithium, 215 to 490ppm Li_2O in average (Munk et al., 2016) and references therein). The alternation of dry and wet periods during the Pleistocene are responsible for the formation of layers of clays (Hectorite), evaporites and associated brines and the variations in the amount of clastic *versus* evaporite sediment fill, combined with faulting, have generated at least six separate brine-bearing aquifers. A combination of hydrothermal activity and leaching from volcanic ash and clays may be the major sources of Li in the aquifers in Clayton Valley, Nevada (Munk et al., 2016). The lithium brines are located within 6 aquifer units of various nature (volcanic ash layers, halite layers, tuffs layers, travertine layers, gravels layers).

Others geological environments are also sometimes favourable to the presence of lithium brines. This is the case for some geothermal fields and some oilfields. For most of the geothermal waters in contact with volcanic rocks or granite in the deep reservoir, rock leaching and hydrothermal alteration (illite or smectite precipitation) are probably the main processes controlling the Lithium concentration. The Na/Li ratios not only depend on the temperature but also on other parameters such as the fluid salinity and origin, or the nature of the reservoir rocks in contact with the geothermal fluids (Sanjuan et al., 2014). European examples include the geothermal field of Cesano (Italy, $\text{Li} = 350 \text{ mg/L}$, volcano-sedimentary), the geothermal field of the Upper Rhine valley (France and Germany, $\text{Li} = 220 \text{ mg/L}$, Triassic evaporites and granite) and the geothermal field of the South Crofty Mine (SW England, $\text{Li} = 125 \text{ mg/L}$, granite).

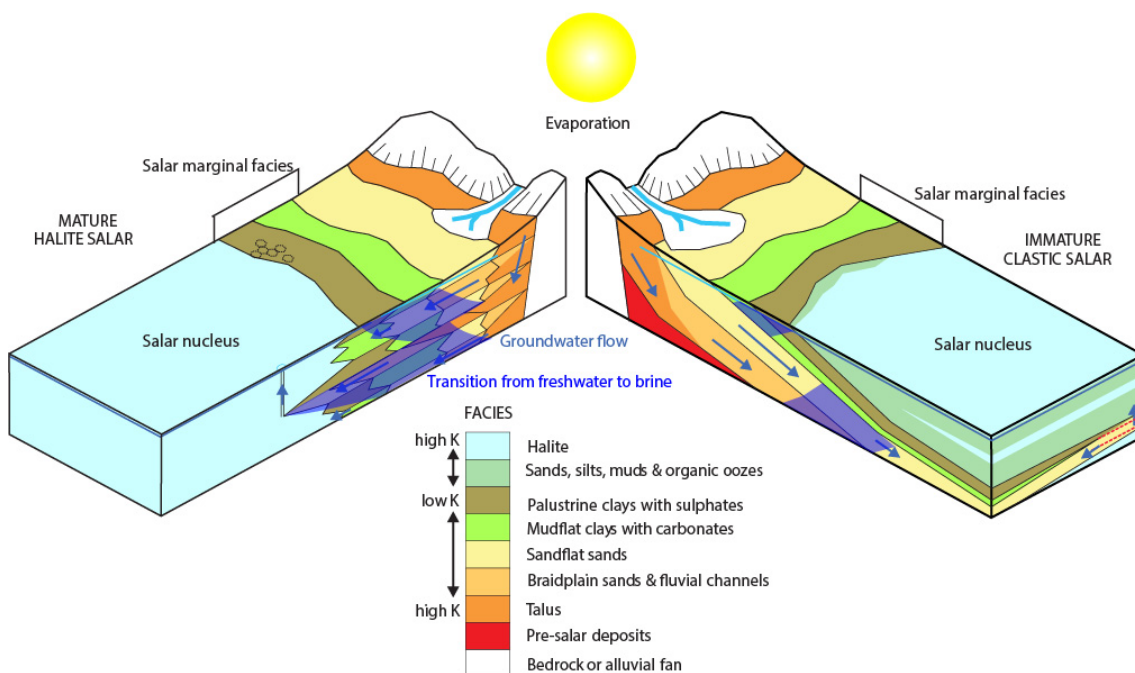


Figure 6: Block models of mature and immature salars showing the distribution of facies and main hydrological components. In the mature model, extension and recession of the marginal facies as a result of tectonism and climate variation lead to the possibility of dilute waters being transferred into the nucleus. In the immature model, while the marginal conditions have been simplified for clarity, the transmission of dilute waters into the nucleus is also possible. K refers to the hydraulic conductivity of the different units. Modified from Houston et al (2011).

3.4.2.1.3 Jadar-type

In 2004, Rio Sava (a subsidiary of the Rio Tinto mining corporation) discovered the Jadar deposit in buried lake basins in Serbia. This deposit, located in the Lopare Neogene sedimentary basin, is now considered as a “non-conventional” world-class lithium deposit through the occurrence of the mineral jadarite ($\text{LiNaSiB}_3\text{O}_7(\text{OH})$, Stanley et al., 2007), a lithium-zeolite. In 2020, the indicated + inferred Mineral Resources (Rio Tinto, 2020) are 2,477,760 t Li_2O (139.2

Mt @ 1.78% Li₂O) including 300,460 t Li₂O of probable ore reserves (16.6 Mt @ 1.81% Li₂O), representing a giant deposit.

The basins are formed as series of inner-montane pull-apart basins during the Oligocene and Early Miocene and were formed during the late stage of the Dinadric orogeny, coeval with the extensional collapse and back-arc extension due to Carpathian slab retreat (Marovic et al., 2002). These basins are typically comprised of clay-carbonate rocks, sandstones and argillaceous rocks formed in a volcano-tectonic depression (subaqueous caldera basin). The early stage of basin formation is marked by lacustrine sedimentation including tuffs from fractionated contemporaneous calcalkaline volcanic rocks. The Lopare basin consists of a relatively large (>20 km long) intramontane lacustrine (paleo)-evaporite basin composed of dolomite, marble, various siliciclastic sedimentary rocks, pyroclastic units and notable oil shales (Obradović et al., 1997). Interestingly, the basement of these basins includes LCT pegmatite and Cretaceous to Miocene granitic intrusions, suggesting local lithium enrichment in the basement (Stojadinovic et al., 2017). The mineralization (Figure 5D) is hosted in a 400–500m thick Miocene sedimentary unit dominated by calcareous claystone, siltstone, sandstone and clastic rocks, unconformably overlying a Cretaceous basement composed of various metasedimentary rocks, limestone, sandstone and granite, including Miocene intrusions. The lithium and borate mineralization occurs as 1.5 to 35m thick stratiform lenses of three gently dipping tabular zones covering a surface area of 3 by 2.5 km. The ore is composed of jadarite-bearing siltstone and mudstone with locally interbedded sodium borate lenses (i.e., ezcurrite, kernite, borax). Jadarite occurs as 1–10mm white and rounded grains, nodules or concretions in the siltstone or mudstone matrix that contains various amounts of calcite, dolomite, K-feldspar, rutile, albite, pyrite, muscovite and ilmenite (Stanley et al., 2007); The Jadarite precipitation is poorly constrained. Some authors suggested that interaction between clastic sedimentary rocks and the surrounding brine—possibly involving hydrothermal devitrification and hydration of andesitic-dacitic pyroclastic material or alteration of clay minerals—may contribute to its precipitation (Stanley et al., 2007; Stojadinovic et al., 2017).

3.4.2.2 Lithium-bearing bauxites

Bauxite deposits can contain various amounts of lithiophorite, cookeite and tosudite (Li rich gibbsite); (Nishiyama et al., 1975). Lithiophorite is the most common Li-bearing manganese oxide mineral in karst bauxites. It occurs in several localities, such as the Halimba, Fenyőfő and Kincsesbanya deposits in Hungary, where aluminum and gallium in bauxite deposits were exploited from the 1950s to recently (Anderson, 2012). The presence of lithiophorite and local cookeite reflect Li enrichment, though this is not systematically evaluated. However, values of up to 0.53% Li₂O within bauxite are known from China (Wang et al., 2019) and the USA (Tourtelot & Brenner-Tourtelot, 1977).

3.4.2.3 Others non-economic lithium mineralisation types

3.4.2.3.1 Mn-(Fe) deposits

Mn-Fe-rich sedimentary units, exploited in the 19th century for their Fe and Mn contents, are a favourable site for secondary Li-oxides such as lithiophorite (e.g., Drogol Mine in Scotland and Clews Gill in England; (Brown et al., 2016). Stratigraphically, they can be subdivided into two distinct units: 1) a reddish siliciclastic host rock, mainly pelite, shale and/or sandstone, enhanced in Mn and Fe relative to the average shale composition; and 2) discontinuous Mn lenses or layers (coticles). The minerals include cryptomelane, goethite, hematite and other manganese oxides including Li-rich lithiophorite, chalcophanite and

pyrolusite. The Li₂O content in lithiophorite is relatively low (1.23 wt% for Li₂O versus 55 wt% for MnO), indicating an uneconomic lithium grade.

3.4.2.3.2 Aalenian black shales from Dauphiné (France)

Aalenian black shales from the Dauphiné region (Isère, France), where cookeite is disseminated in black shales and in tension gashes crosscutting the shales (Jullien & Goffé, 1993). For the latter occurrence, values (Henry et al., 1996) are in the range of 9 to 1 847 ppm Li₂O with an average of 441 ppm Li₂O (n=10). These lithium occurrences are symptomatic for local conditions allowing minor enrichment, implying that they are not economically significant regarding their Li content.

4 Cobalt

4.1 Properties of cobalt

Cobalt is a transition metal with an atomic number of 27, situated between iron and nickel in the periodic table. Average crustal abundances of cobalt are similar to other transition metals (e.g., copper, zinc and nickel) at 15-30 ppm, with higher concentrations in MgO-rich ultramafic rocks (up to 100 ppm, or 0.01 %) (Taylor & McLennan, 1995; Wedepohl, 1995). Pure metallic cobalt does not occur on Earth, most commonly it is combined with iron, nickel, copper, sulphur and arsenic to form sulphide, sulpharsenide and arsenide minerals, but is also found as carbonate and hydroxide minerals, and also as a minor to trace component in a number of other minerals (Table 4).

Mineral	Formula	Co content (wt. %)	Mineral	Formula	Co content (wt. %)
Cobalt sulphides			Co-containing sulphides		
Co-pentlandite	(Co,Ni,Fe) ₉ S ₈	10-60	Pentlandite	(Ni,Fe) ₉ S ₈	<0.5-5
Linnaeite	Co ²⁺ Co ₂ ³⁺ S ₄	40-60	Millerite	NiS	0.2-2
Carrolite	Cu(Co,Ni) ₂ S ₄	35-38	Violarite	Fe ²⁺ Ni ₂ ³⁺ S ₄	0.2-3
Siegenite	(Ni,Co) ₃ S ₄	13-26	Pyrite	FeS ₂	<0.01-3
Cattierite	CoS ₂	42-48	Pyrrhotite	Fe _(1-x) S	<0.01-0.3
As-S minerals			Other		
Cobaltite	(Co,Fe,Ni)AsS	20-35	Erythrite	Co ₃ (AsO ₄) ₂ 8H ₂ O	30
Alloclasite	(Co,Fe)AsS	10-29	Heterogenite	CoOOH	64
Glaucodot	(Co,Fe)AsS	10-20	Kolwezite	(Cu,Co) ₂ (CO ₃)(OH) ₂	30
Gersdorffite	(Ni,Fe,Co)AsS	0-10	Sphaerocobaltite	CoCO ₃	50
Arsenopyrite	FeAsS	<0.01-5	Asbolane	(Ni,Co) _{2-x} Mn(O,OH) ₄ ·nH ₂ O	>4
Safflorite	(Co,Fe)As ₂	10-30	Lithiophorite	(Al,Li)Mn ⁴⁺ O ₂ (OH) ₂	~7
Skutterudite	(Co,Ni)As ₃	20-30			
Löllingite	FeAs ₂	<0.01-5			

Table 4 Important cobalt minerals and cobalt-containing minerals in ore deposits.

In geological processes cobalt generally behaves in similar way to nickel, but in various ore forming processes cobalt may follow copper or other metals. Although cobalt is found in a number of different ore types associated with various other metals, it rarely forms deposits where it is the main commodity. Globally the three most important Co-producing ore types are stratiform sediment-hosted Cu-Co deposits (SSHC) found especially in the Central African Copperbelt stretching from Zambia to DRC, lateritic Ni-Co deposits occurring in equatorial latitudes in e.g., Australia, New Caledonia, Brazil and Indonesia, and magmatic Ni-Co deposits, which is the most widespread deposit type. Other, less important deposit types that can contain cobalt are volcanogenic Cu-Zn deposits (VMS), metasediment-hosted Co-Cu-Au deposits, Iron-oxide Cu-Au (IOCG) deposits, black-shale hosted deposits, skarn and replacement deposits, and polymetallic vein deposits (Slack et al., 2017).

In a European context the most important deposit types are magmatic Ni-Cu deposits and VMS deposits prominent especially in the Nordic countries (Finland, Norway and Sweden), vein type polymetallic deposits, which are widespread across Europe, although generally small in scale, and lateritic deposits in the Balkans and also Ukraine. The Kupferschiefer Cu-deposits in Poland can be classified as SSHC-type deposits, but they contain very low Co contents. The giant Sotkamo (Talvivaara) black schist hosted Zn-Ni-Cu-Co deposit in Finland could also be classified as SSHC-type deposit but the genesis and metal spectrum are quite different from SSHC deposits and should be classified as its own type, along with some other black schist/shale hosted or sulphidic shale/schist hosted deposits elsewhere, mainly in China and north America.

4.2 Cobalt behaviour in ore forming processes and genetic types.

In addition to classifying cobalt deposits by their host-rock type or metal association, they can be classified based on their formation process or genesis. Basically, all different Co-containing deposits can be classified to three main types, based on their genesis: 1) Magmatic Ni-Cu-Co±PGE deposits, 2) Laterite deposits, and 3) Hydrothermal deposits, which is the most varied type.

4.2.1 Cobalt behaviour in magmatic processes (magmatic Ni-Cu-Co deposits)

Cobalt is a ubiquitous minor constituent in magmatic Ni-Cu deposits. These types of deposits are always hosted by distinct type of magmatic formations, i.e. relatively MgO-rich intrusions or extrusions (lava flows). The magmas responsible are generated by the partial melting of the mantle, thereby acquiring metals, especially nickel, hosted in the mantle phases. For the formation of the requisite magma with a minimum MgO content of ~8 % MgO, 10-15 % of the mantle material must melt. Komatiitic magmas contain up to 30 % MgO and require up to 50 % melting of the mantle. With increased percentage of melting the resultant magma contains higher amounts of MgO and FeO but also Ni and Co, whereas the content of Cu, S and platinum group elements (PGE) reach a maximum at 20-25 % melting and their concentrations are diluted at higher degrees of melting (Naldrett, 1999).

The hot and less dense magma rises upwards and either forms magma chambers within the Earth's crust or erupts on the surface. Magma chambers within the crust start to cool and eventually crystallize as mafic-ultramafic (MgO-rich) intrusive rock types, which can host Ni-Cu-Co-PGE sulphide deposits. The formation of these sulphide deposits requires the separation of a sulphide melt from the silicate magma. Generally, for the formation of an economic deposit, the magma has to acquire external sulphur by assimilating sulphur containing rocks as it rises up through the crust and forms a magma chamber. The addition of sulphur causes sulphide saturation and formation of a dense sulphide melt, which collects metals from the silicate melt.

The melt then sinks to the bottom of the magma chamber and forms a high-grade sulphide ore, typically with a few precents of Ni and/or Cu and 0.01-0.2 % of Co. Typically, these types of ore consist of a massive ore, a matrix ore and disseminated ore, at respectively lower grade. In some cases, the sinking sulphide droplets can get trapped with the crystallizing silicate phases, forming a lower grade disseminated sulphide deposit. The metal content of the sulphide melt depends on several factors. Each metal has different partitioning coefficient (D value) between the silicate and the sulphide melt. Platinum group elements, especially platinum and palladium have very high D values, in the range of 60 000 to 100 000, meaning that they have high preference to the sulphide melt. Base metals have much lower values, Cu 500-1500, Ni 300-1000 and Co 20-80 for Co (Barnes et al., 2005; Naldrett, 2011). For effective collection of metals from the silicate melt, a turbulent environment is favoured where the sulphide melt can “mop” metals form a large volume of silicate melt, this results in a large R-factor, which the ratio of silicate melt to sulphide melt. Another factor that can affect especially the Ni content is whether olivine has been crystallizing before sulphide melt generation, as olivine incorporates significant Ni, removing Ni from the silicate melt and making it unavailable for the sulphide melt.

Cobalt rarely forms its own minerals in these types of deposits; most of the cobalt is incorporated in the main Ni-mineral pentlandite ($(\text{Ni,Fe})_9\text{S}_8$), which typically contains 0.5-3 % Co. The rest is usually hosted in the main Fe-sulphide pyrrhotite at much lower concentration (0.05-0.2 %). As a consequence, the overall Ni grade of the deposit also controls the Co grade, which is illustrated in the Figure 7 below. Some of the Co and Ni are also retained in the crystallizing silicate minerals, especially olivine and are thus not available for possible extraction.

Magmatic Ni-Cu-Co deposits have highly variable total tonnage and metal grades, varying from 0.1 Mt to 500 Mt in size (e.g.(Naldrett & Naldrett, 2004). Small to medium-sized (0.2-15 Mt) magmatic Ni-Cu-Co deposits have been mined in the past in Europe, mostly in Finland and Sweden. The Aquablanca mine in Spain was in operation between 2004 and 2015 (Horn et al., 2021). Currently, the Kevitsa deposit (128 Mt reserve and 175 Mt mineral resources) in northern Finland is to only operating mine, producing some 11 000 t of Ni, 27 000 t of Cu and 500 t of Co in concentrates (Boliden, 2020).

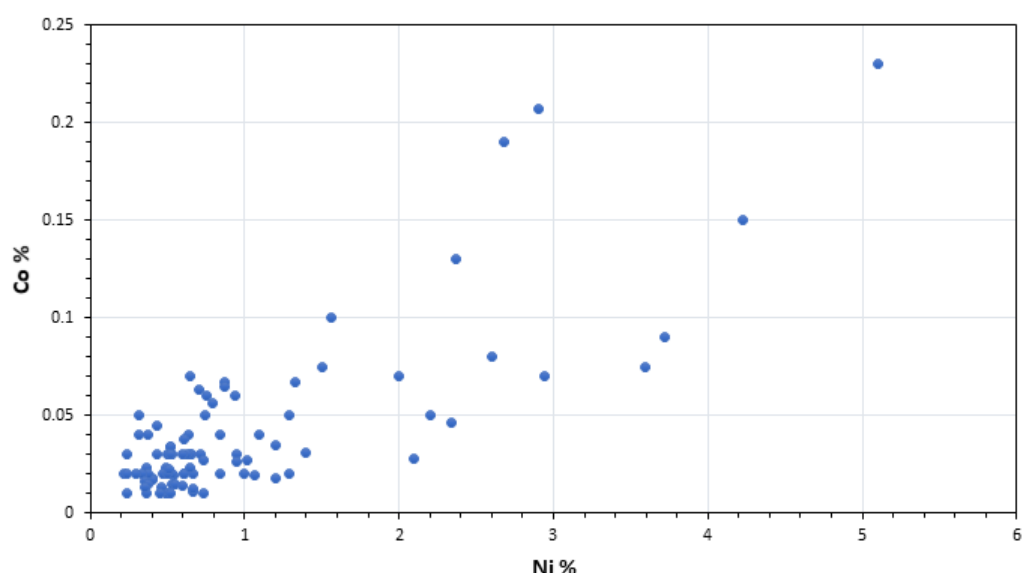


Figure 7 Global examples of average Ni and Co grades of some Ni-Cu deposits.

4.2.2 Cobalt behaviour in hydrothermal processes (sediment-hosted Cu-Co, vein-type and VMS deposits)

Hydrothermal processes and hydrothermal fluids can deposit a wide variety of different metals, including base metals (Fe, Mn, Cu, Zn, Pb and Co) and precious metals (Pd, Au, Ag) in a variety of geologic and tectonic settings. A hydrothermal fluid is an aqueous (water based) solution with a temperature range of 50 to > 500°C containing various solutes (elements and compounds), which are precipitated due to changes in the properties of the fluid, such as temperature, salinity, pressure, pH, etc. The water in hydrothermal fluids can be seawater, meteoric (fresh surface water), connate (water trapped in sediments), metamorphic, juvenile (water derived from the interior of the Earth) or magmatic (Pirajno, 2008).

In order for a water-based solution to be able to carry and transport metals, it must contain sufficient amounts of complexing ligands such as chloride (Cl^-) and sulphide (HS^- and H_2S). Sea water and magmatic fluids inherently already contain these ligands, and in many cases also connate water in sediments deposited in marine environment, whereas surface waters need to dissolve them from surrounding rocks. Metamorphic fluids are generated by dehydration of water containing minerals as temperature increases in metamorphic events. The hot fluid dissolves existing sulphide minerals in the rocks acquiring sulphur compounds for metal transport, but generally they have low Cl^- concentration. Most base metals are carried as chloride complexes in hydrothermal fluids, whereas Au is mostly carried by sulphur complexes. Cobalt can form both sulphur complexes, which are important in lower temperatures (<200-250°C), whereas Cl^- complexes dominate at higher temperatures (Migdisov et al., 2011; Seward et al., 2014) and at higher Cl^- concentration (i.e., brines).

4.2.1.1 Cobalt behaviour in sediment-hosted Cu-Co deposits

Stratiform sediment-hosted Cu-Co deposits (SSHC) are the most important global source of cobalt accounting for 63% of cobalt mine production in 2017 (Petavratzi et al., 2019). They have variable tonnage and grades, ranging from 1 Mt up to 700 Mt, with Cu grade varying from 1 to 5% and Co grades varying from <0.01% to 1.1% with a median grade of 0.3 % in 170 deposits worldwide (Taylor et al., 2013). A large proportion of SSHC deposits occur in the Central African Copperbelt stretching from north-west Zambia to southern DRC. Deposits in DRC tend to have higher Co contents than Zambia or elsewhere with several deposits containing over 0.5% Co. Cobalt occurs mainly as carrollite, cattierite and linnaeite in unweathered parts of deposits, while heterogenite and asbolane occur in the upper weathered parts of deposits.

SSHC-type deposits occur in intracratonic sedimentary basins, often related to failed continental rifts developed in equatorial areas, suitable for the development of red beds. In many cases, the basins are related to supercontinent break-up during Neoproterozoic (Rodinia, 1000-720 Ma, Katanga basin DRC) and late Permian (Pangea, 250-175 Ma, Zechstein Basin, Kupferschiefer Formation). Intracratonic basins with SSHC deposits commonly contain several sequences of subaerial red bed sediments, more reducing (organic carbon containing) sediments deposited in shallow marine environment and sulphate- and halite- (salt minerals) bearing evaporites developed in tidal environments and associated volcanic rocks. The oxidized red beds contain hematite and goethite, which is thought to have adsorbed Cu and are thought to be essential for the genesis of SSHC deposits. Oxidized basinal brines, i.e., high salinity fluids with temperatures at 75-220°C can be generated during diagenesis and lithification of the sedimentary basin. They can be derived from trapped seawater, residual bittern brines

(evaporitic brines), brines generated by evaporite dissolution. These brines leach copper and other metals from synrift red beds and mafic volcanic rocks and migrated along faults upwards or outwards along faults due to diagenetic and/or metamorphic events. Metal deposition was caused by interaction with reducing, organic carbon containing sediments, or hydrocarbons or hydrogen sulphide (H₂S) present in porous sandstones (e.g., (Hitzman et al., 2010; Taylor et al., 2013). It has been postulated that cobalt-rich deposits are related to the occurrence of mafic intrusions in the basement, which were the source of Co-enriched fluids (Hitzman et al., 2017).

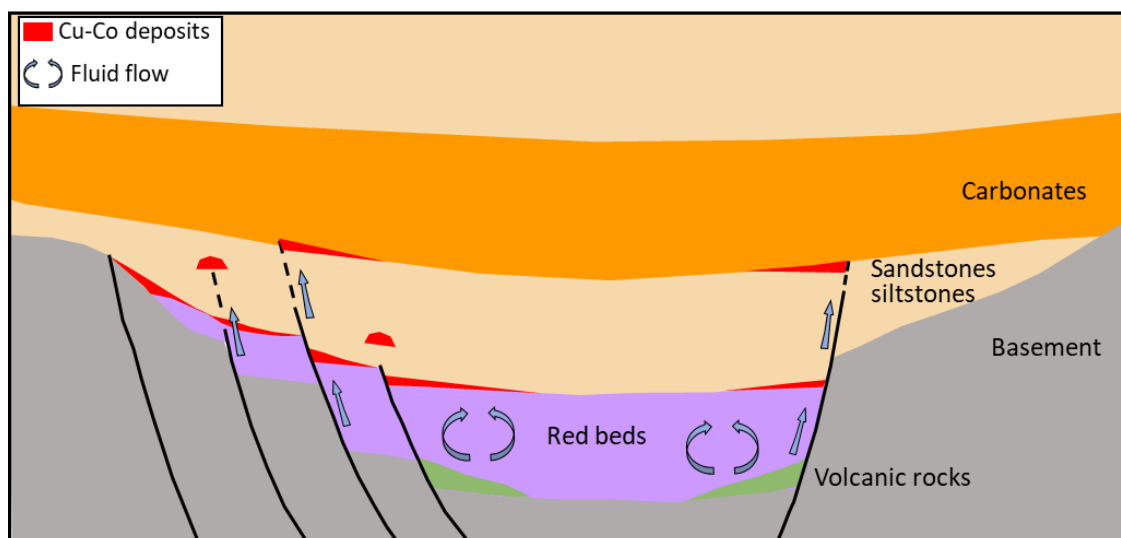


Figure 8 Schematic cross section of intracratonic rift basin and associated SSHC-type Cu-Co deposits. Modified after Hitzman et al., 2010. Schematic cross section of intracratonic rift basin and associated SSHC-type Cu-Co deposits. Modified after Hitzman et al., 2010.

4.2.1.2 Cobalt behaviour in vein-type deposits (5-element vein deposits)

Vein-type deposits containing silver, bismuth, cobalt, nickel and arsenic, often called 5-element vein deposit, occur throughout southern and central Europe, but are rare in Fennoscandia. The veins contain variable amounts of these elements or they can be dominated by some element, such as in the Kongsberg Ag-deposit in southern Norway. They can also contain uranium, copper, and antimony. The veins can also be “telescoped” with Ni-Co-As phases occurring in parts of the vein, and base metal (Cu-Zn-Pb) sulphides occurring in other parts. The host rocks to the veins can be crystalline basement rocks (intrusives, metamorphic rocks) or sedimentary formations. The vein can be several hundred of meters in length and cm-scale to a few meters in width. As the metal grades can be quite high (up to several percent of Ni and Co), they were important sources for many elements, starting from the Middle Ages, especially in Germany (Kissin, 1992). Formation 5-element vein type deposits in Europe are generally ascribed to Hercynian (~400-300 Ma, Pangea formation) and Alpine (<120 Ma, collision of African plate with Eurasian plate) orogenies (Horn et al., 2021).

The 5-element veins, represent hydrothermal deposit type where the metals were carried by highly saline (typically 20-50 % NaCl equivalent), oxidised brines, which developed from sedimentary brines, or represent metamorphic or magmatic fluids, leaching metals from fluid source rocks or derived them from the source intrusions (Kissin, 1992; Scharrer et al., 2019), although the magmatic origin is currently mostly discarded (Scharrer et al., 2019). Studies indicate wide temperature regime during deposit formation, probably related to multistage formation by several fluid pulses, with temperatures ranging from as low as 50°C to a high of 450°C. Early-stage mineralization is quartz-oxide dominant and can contain U, followed by main

stage mineralization with native elements (Ag, Bi, As) and Ni-Co arsenides and sulfarsenides, with late stage base-metal sulphide and carbonate stage. Deposition of metals is thought to be related to reduction of the fluid by hydrocarbons or methane, or reaction with carbonaceous of black shales or with Fe-rich or sulphide bearing formations (Kissin, 1992; Scharrer et al., 2019).

4.2.1.3 Cobalt behaviour in sea floor hydrothermal system (Cu-Zn-Pb VMS deposits)

Volcanogenic massive sulphide (VMS) deposits are important sources of copper, zinc and lead, and can also contain significant silver and gold, and more rarely also cobalt. Generally, base metal concentrations are in the range of 1 to 5 %, with 0.2-1 ppm gold and 10-50 ppm Ag. Cobalt grades are variable but typically from <100 ppm to a few hundred ppm. In some, relatively rare cases cobalt grades can reach close 0.1 % and even more rarely up to 0.2-0.4 % (Slack et al., 2017). Higher cobalt grades are usually found in Besshi-type or the siliciclastic-mafic type of (Shanks & Thurston, 2012) such as the Besshi deposits of Japan or Windy Craggy in Canada and also in some ophiolite-hosted deposits in the Urals, China (Dur'ngoi) and Finland (Outokumpu-type Cu-Zn-Co-Ni deposits) (Slack et al., 2017). However cobalt grades are not routinely reported from VMS deposits and also the host phases are not well known. Reported data indicate that in many cases large proportion of Co is hosted in pyrite and pyrrhotite, with grades of 1 % and 0.1 % reported from Windy Craggy. Similar Co grades occur in pyrrhotite from Besshi deposit where more Co-rich phases (Co-rich pentlandite, Co-bearing mackinawite, and cobaltite) have also been reported (Peter & Scott, 1997). Several of the Finnish Outokumpu-type VMS deposits have been mined over the years and they also produced Co-concentrate. In the deposits, cobalt is mainly hosted by cobaltpentlandite, which accounts 50-80 % of the Co, with the rest hosted in Fe-sulphides and trace cobaltite (Kontinen et al., 2006; Peltola, 1978; Törmänen & Tuomela, 2021). The age range of VMS deposits is from early Archean (3550 Ma) to Miocene deposits of Japan. VMS deposits are also currently forming on the seafloor, with more than 500 deposits known (Shanks & Thurston, 2012).

VMS deposits are formed at or below seafloor at variable tectonic settings, the most important being seafloor spreading centres such mid-ocean ridges (e.g., Mid-Atlantic Ridge), island arcs and back-arcs in subduction settings, such as the western Pacific “ring of fire” and sea mounts. VMS deposits can form anywhere on the seafloor where there is: 1) a sufficient source of heat to drive the hydrothermal circulation, usually in the form for magma chamber below and 2) pathways for cold seawater to penetrate into the crust below to sufficient depths to heat up. These can be e.g., faults zones associated with spreading centres, and 3) sufficient water depth to prevent significant boiling before the hot fluid exits to the seafloor and precipitates metals in the form of sulphide minerals. A minimum depth of about 1500m is generally required. Figure 9 shows a schematic cross section of a seafloor hydrothermal system, where cold sea water penetrates to the lower part of oceanic crust, is heated up and becomes more acidic by Mg-precipitation and wall-rock alteration reactions, facilitation the uptake of metals and sulphur from the sub-seafloor bedrock. The generated hydrothermal fluid has a temperature of > 350°C. The hot fluid rises up along high permeability zones such as fault zones along spreading centres. Upon exiting on the seafloor, the fluid mixes with cold sea water and the metals contained in the fluid are precipitated on the seafloor. More saline and lower temperature fluids can form pools in depressions on the seafloor, with more efficient metal retention in the sulphide deposit (Hannington, 2014; Hannington et al., 2005).

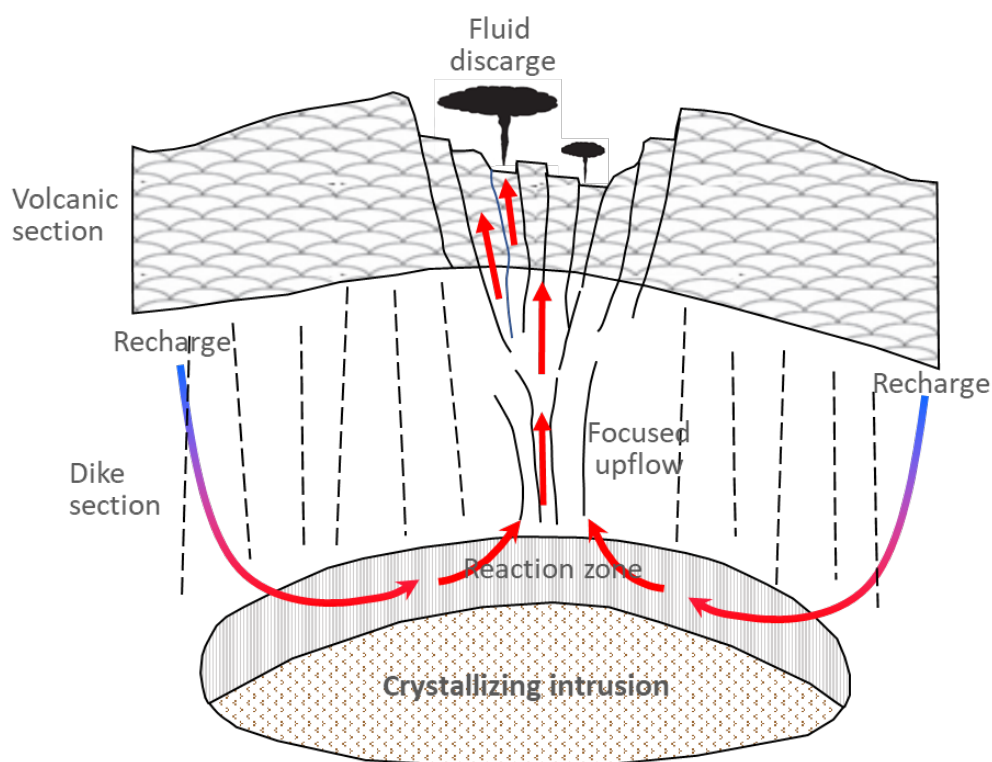


Figure 9 Schematic cross section of a typical submarine hydrothermal system. Vertical scale exaggerated. Modified after Hannington, 2014.

The metal content of the high-temperature fluid is mostly controlled by its temperature, salinity and pH, with high-T and salinity, and lower pH increasing metal solubility in the fluid. Iron and manganese are the most abundant metals in modern high-T hydrothermal fluids with 250 ppm and 50 ppm, respectively, with much lower Cu (1-10 ppm) and Zn (1-10 ppm, locally up to 50 ppm) contents, and generally very low Co contents below 0.1 ppm. A few modern seafloor deposits contain elevated Co contents such as the Rainbow (0.42% Co) and Ashadze-1 (0.29% Co) at Mid-Atlantic Ridge, and Daxi (0.1-0.34% Co) and Edmond (up to 0.2% Co) vent fields at Central Indian Ridge and Carlsberg Ridge, respectively (Hannington, 2014; Wang et al., 2021; Wu et al., 2016). Cobalt enrichment in these sites is related to a combination of high fluid temperature (>350°C) and/or salinity (~2 x sea water salinity, i.e., ~7% NaCl equivalent), reduced fluid chemistry and often also more ultramafic seafloor (Ocean Core Complexes, OCC) associated with many of these deposits, providing more Co-rich substrate for fluid leaching (e.g., Fouquet et al. 2010). It has also been proposed that additional metals could be added by high-salinity magmatic brines originating from subvolcanic intrusions e.g. (Hannington, 2014), 2014).

4.2.3 Cobalt behaviour in supergene processes (lateritic Ni-Co deposits)

Laterites are regoliths that are produced by chemical weathering of the bedrock at Earth's surface in subtropical to tropical climates with warm temperatures and seasonally high rainfall over long time periods (millions of years). Other factors affecting laterite development include topography and tectonics: high relief increases erosion on the surface and removal of the regolith, as does tectonic uplift, whereas tectonic stability in stable cratonic areas favour planation and formation of deeper lateritic deposits. Faulting of the bedrock and development of cracks and cleavage improve and speed up alteration. Bedrock composition also affects the

rate of chemical weathering with ultramafic MgO-rich rocks being 2-3 times more susceptible compared to more SiO₂ -rich rock types, such as granite (Elias, 2002).

Lateritic Ni-Co deposits are formed due to chemical weathering of MgO or olivine rich, ultramafic rock types, such as ophiolites (tectonically transported slivers of sea floor), ultramafic olivine and pyroxene-rich intrusions and serpentinites (metamorphic equivalents), and komatiites (MgO-rich volcanic formations). These types of rocks have relatively high Ni and Co-contents (0.1-0.4 % Ni and 0.01 % Co) to begin with, hosted mostly by silicate minerals, which can be upgraded by 3 to 30 times by the lateritisation process. In the lateritization process, silicate minerals are altered and/or broken down and some of their chemical components, such as Ni and Co into groundwater, which can then be adsorbed by Fe-Mn oxyhydroxides, clays and other secondary minerals that are stable in the weathering environment. Lateritic Ni-Co deposits are usually 10-40 m thick and typically contain ~1% Ni and 0.01-0.2 % Co, with typical Co-contents ranging from 0.05 to 0.1 % (Elias, 2002; Slack et al., 2017).

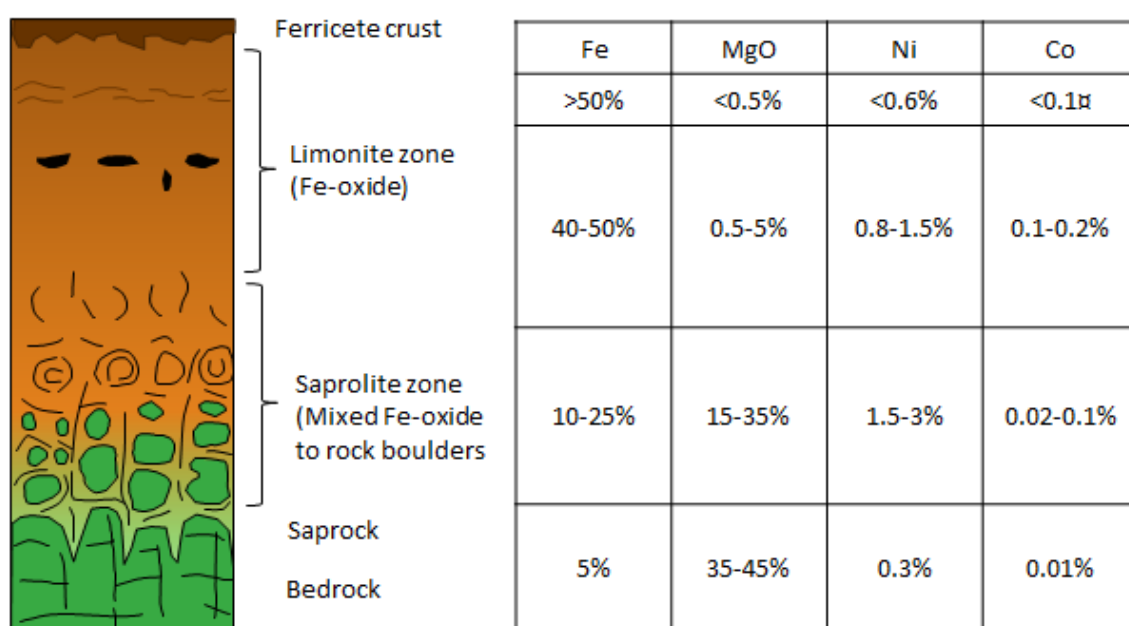


Figure 10 Schematic laterite profile developed on ultramafic rock with approximate chemical composition on right (modified after Elias 2002).

Most nickel-cobalt laterite deposits are mid-Tertiary (30 Ma) to Holocene (i.e., forming currently) in age and can be classified into three main sub-types: Oxide, Mg-silicate, and clay silicate types. Figure 10 is a schematic representation of an oxide laterite deposit and associated chemical changes with different zones. Oxide deposits typically form on olivine-rich rock types. They are often capped by a hard Fe-rich crust (ferricrete or iron crust) followed by the so-called limonite zone composed of Fe-oxyhydroxides (goethite) and hematite as well as manganese oxides (e.g., asbolane, lithiophorite), which have adsorbed Ni and Co, and usually contain the highest Ni and Co concentrations. Below the limonite zone is the saprolite zone with a mixture of Fe-oxyhydroxides, partially oxidised ultramafic material and relatively fresh unaltered ultramafic boulders. The Mg-silicate type generally forms on metamorphosed ultramafic rocks, serpentinites. They have a thinner limonite zone and a thicker lower saprolite zone composed of serpentine, clays, and hydrous low-crystallinity Ni-Mg silicates. These types of lateritic deposits contain the highest Ni grades of up to 5 % Ni but moderate Co grades of ~0.1 %.

type deposits are found in stable cratonic areas and in somewhat cooler or dryer climates. Nickel and cobalt occur in a clay mineral zone in the upper parts of the laterite, beneath a relatively thin oxide zone. Ni and Co are hosted by clay minerals such as nontronite and saponite. Typical Ni grades are 1-1.5 % and Co grades are 0.03-0.1 % (Butt & Cluzel, 2013; Elias, 2002; Slack et al., 2017).

In Europe, lateritic Ni-Co deposits occur in the Balkans; Albania, Bosnia and Herzegovina, Greece, Kosovo, North Macedonia and Serbia, some of which are in operation (e.g., Ržanovo in N. Macedonia and Gllavicë in Kosovo) or were recently in production (Greece deposits) but cobalt has not been produced from these deposits (Horn et al., 2021). Most of these deposits are related to Mesozoic to Cenozoic (20-200 Ma) ophiolites, the Western and Eastern ophiolite belts and were formed by two lateritic weathering phases during late Jurassic to Early Cretaceous (150-130 Ma) and Eocene to Miocene (50-10 Ma), under subtropical to tropical climate conditions (Horn et al., 2021). Lateritic Ni-Co deposits occur also in Ukraine and some in Poland and Slovakia.

5 Graphite

Graphite is a polymorph of pure elemental carbon, after helium and hydrogen the third most abundant element in the universe, and the most important element for life and biological processes and it is perhaps the most diverse of all elements in the periodic table. Carbon its formation and properties has been described in the very readable book “A symphony in C” by (Hazen, 2019). Different from lithium and cobalt bearing minerals, graphite is a quite a common mineral in many geological settings, but like lithium and cobalt it is rare to find enrichments that are economically interesting. Being the sole element in a single mineral, the geology of graphite is naturally much simpler than that of lithium and cobalt. In a geological context studies of graphite occurrences are much rarer, compared to those on lithium and cobalt. In addition most graphite mines are privately owned, making information on production much less available than for public metal producing mines.

In geological material elemental carbon occurs in two minerals graphite and diamond. The difference is well described in any introductory text in mineralogy and will not be discussed here.

5.1 Graphite deposit types, formation and characterization.

5.1.1 Scientific classification of graphite and carbonaceous material

There is a difference in the scientific and industrial classification of graphite and carbonaceous material. Scientists base their distinction and classification of graphite relative to other carbonaceous materials on vitrinite reflectance, XRD and Raman spectroscopy measurements and divide graphitic material into semi-graphite and graphite (Kwiecińska & Petersen, 2004) for review. The industry on the other hand uses the grain size of the graphite crystals as the main parameter for distinction between flake and amorphous graphite.

Graphite is well crystallised a stable form of carbon occurs on the surface and in the deep crust. Compared to the occurrence of poorly crystallised, disordered carbonaceous material, proper graphite *sensu stricto* is relatively rare. In the 1950s investigators got the understanding of the processes involved in the conversion of carbonaceous material into crystalline graphite. The

process was called graphitization (Franklin, 1951). Franklin identified two types of carbonaceous matter that evolved from biological organic matter in early stage of diagenesis and metamorphism, graphitizable and nongraphitizable carbon. This distinction is still valid although advancement in analytical methods have resulted in a refinement in the understanding of the differences and processes involved (Buseck & Beyssac, 2014).

In geological environments the processes operating during graphite formation can somewhat simplified be describes as follows: The process is two stage (figure 11).

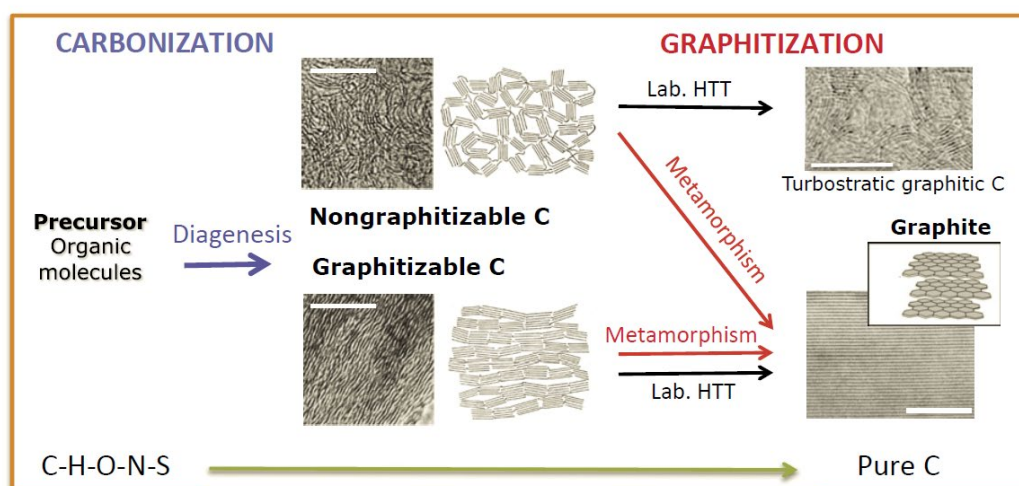


Figure 11 The process of graphite formation from diagenesis to fully crystalline graphite sees (Buseck & Beyssac, 2014) for details.

The first a stage of carbonization which occur under diagenesis involves cracking and decomposition of the organic matter to produce hydrocarbons and leaves behind a solid carbonaceous residue. This residue is gradually enriched in carbon and the hydrocarbons migrate; the trapped residue is converted to graphite with advancing metamorphism. Laboratory testing indicate that all organic matter is converted to graphite at temperatures above 700° C (Buseck & Beyssac, 2014)

If the migrating hydrocarbons are trapped in the rock **flake graphite occurrences** (see below) will be formed in situ. If it becomes part of hydrothermal solutions, carbon may be deposited syngenetically in veins and **Vein graphite types** (see below) is the result.

The International Committee for Coal and Organic Petrology (Kwiecińska & Petersen, 2004) have developed a classification for graphite, semi graphite, natural coke, natural char (Kwiecińska & Petersen, 2004). The following methods is used to distinguish these variants of organic matter:

1. Vintrenite reflectance
2. Raman spectroscopy
3. XRD diffractormetry
4. TEM microscopy

The two latter (XRD and TEM) measure essentially the same but on a different scale. Table 5 show the difference the 002 crystal lattice spacing and reflectance between graphite semi graphite and anthracite

Material	XRD (002) (Å)	Reflectance % Rmax
Graphite	3.354-3.337	< 9.
Semi graphite	3.37-3.38	6.5-9.0
Meta antracite	3.38-3.40	<6.5
Antracite	>3.40	<5.0

Table 5 Distinction of graphite, semi graphite, meta antracite and antracite with XRD and vitrinite reflectance (compiled from (Kwiecińska & Petersen, 2004)).

The (002) lattice value of 3.354-3.337 Å seem to be a reliable indicator for the formation of graphite as well as an indication of metamorphic grade (Wada et al., 1994).

5.1.1.1 Raman spectroscopy

Raman spectroscopy is a fast and popular method for distinguishing the different varieties of organic matter and can be done with minimum of sample preparation. Wopenka and Pasteris (Wopenka & Pasteris, 1993) showed that there is a systematic evolution of the Raman spectra of graphite relative to the degree of metamorphism (Figure 12.) With metamorphic degree there is a systematic shift in peak size and position of the primary D and G band and the secondary bands. Beyssac et al calibrated this variation (Beyssac et al., 2002) and developed a Raman spectroscopy carbonaceous thermometer (RSCM thermometry) See also (Buseck & Beyssac, 2014) for review.

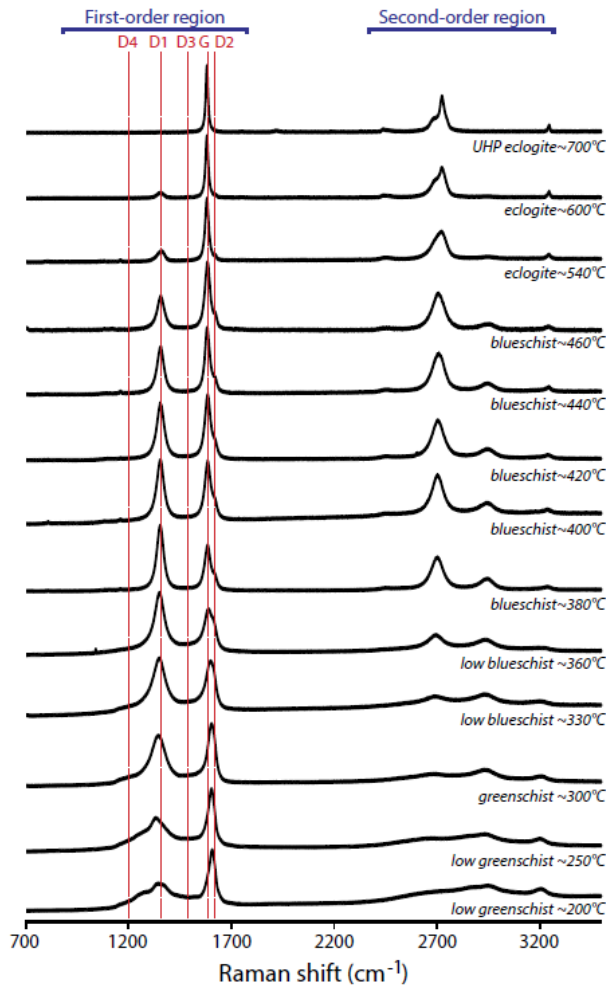


Figure 12 Raman shift in relation to metamorphic grade in graphite from (Buseck & Beyssac, 2014).

5.1.1.2 Carbon isotopes

Carbon isotopes is an important tool for distinguishing the sources and processes for graphite formation

The carbon isotopes in graphite usually show a $\delta^{13}\text{C}$ in the range -35 to -20 because of its biogenic source. Modification of the isotope signature can occur due to processes like: a) progressive enrichment due to graphitisation and b) exchange of carbon with carbonates and c) recrystallisation at a higher temperature (Schidlowski, 2001).

The graphite originating from a biological precursor without any later modification will display a light isotope signature. This is the case for most graphite occurrences.

If the carbon originates from the mantle, from methane or from decarbonisation of carbonates the graphite will then be deposited as vein graphite and can display a heavy carbon isotope signature with $\delta^{13}\text{C}$ in the range -7 to about 0. This is illustrated in Figure 13 from (Luque et al., 2012).

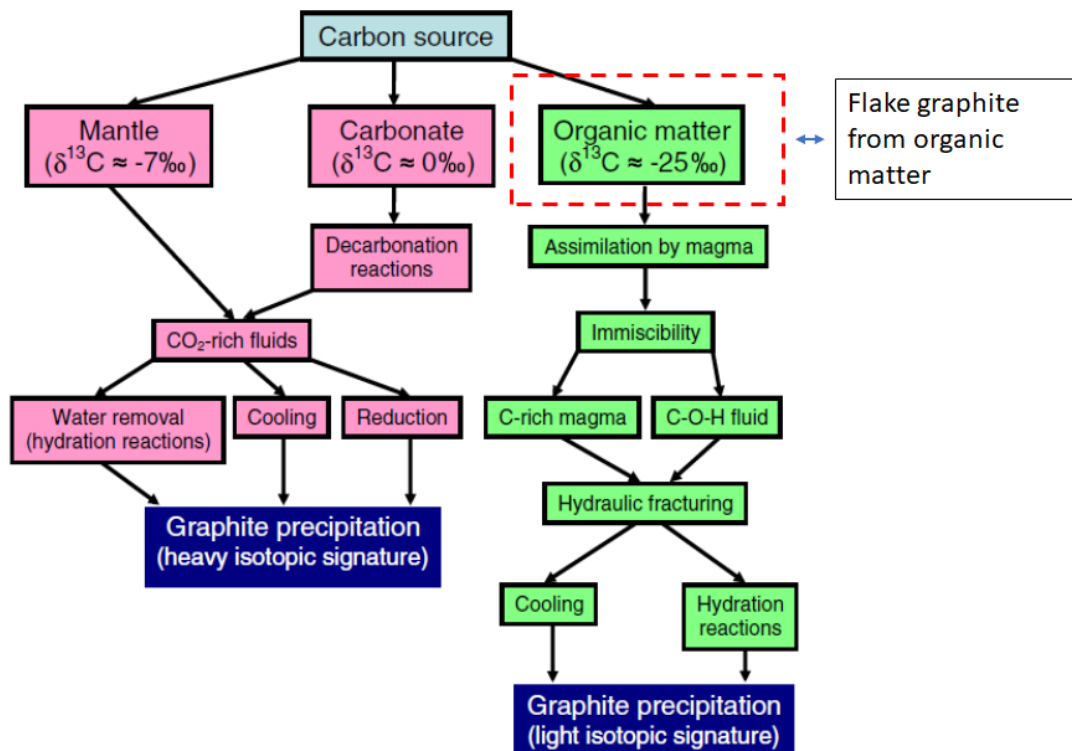


Figure 13 The carbon isotope signature in relation to source and process of formation (modified from (Luque et al., 2012))

5.1.2 Industrial classification of graphite types

The industry divides natural graphite and the occurrence types of graphite into the following groups see (Harben & Kužvart, 1997) for review:

- A) **Flake graphite:** Flake graphite is graphite formed in metasedimentary rocks of high metamorphic grade. These deposits are characterized by the presence of flakes of individual graphite crystals in variable grain size. Traditionally the coarser flakes yield more valuable ore, and the carbon content can vary from 2-3 % up to more than 30 %. The metamorphic grade of the graphite bearing rocks are either high amphibolite or granulite facies.
- B) **Amorphous graphite:** The term amorphous graphite is misleading, and micro crystalline graphite is more a correct description. This type of graphite is formed from coal deposits altered by contact metamorphism, or from low metamorphic grade organic-rich shales. About 50 % of the world's production comes from of this deposit type. This ore type typically occurs as masses of graphite rich rock. Worldwide amorphous graphite deposits have in general higher carbon (graphite) content than flake graphite deposits (Robinson et al., 2017).
- C) **Vein or lump graphite;** this is a special type of graphite deposit that are only being mined in Sri Lanka. They are shown to be formed by processes that involve the interaction of CO₂, CO, CH₄ and H₂O during granulite facies metamorphism. Although

these deposits are only mined on Sri Lanka, their occurrence is not uncommon (Luque et al., 2014).

Most of Europe's and the world's graphite occurrences have their carbon and graphite from a biogenic source. Whether the graphite crystallizes to form a flake or amorphous graphite deposits is determined by the subsequent metamorphism. In general, high grade amphibolite or granulite metamorphism creates flake graphite deposits and lower metamorphism results in an amorphous type. However, it is not uncommon for a single mine to produce grain size fractions that are sold on the market for flake graphite and amorphous graphite, depending on the particle size of the carbon.

World wide amorphous graphite deposits are the source for about 40 % of the world's production. 58% comes from flake graphite deposits and 2% from veins deposits (Olson, 2020). In Europe flake graphite is produced from mines in Norway and Ukraine and amorphous graphite from two mines in Austria. A relative high proportion of the graphite occurrences in Europe are unclassified, the lack of detail studies make it impossible to group them into either flake- or amorphous deposits.

5.1.2.1 Properties, use and quality requirements

Graphite is an excellent conductor of heat and electricity; stable over a wide range of temperatures, and highly refractory, with a high melting point; it is compressible and malleable and resists chemical attack and thermal shock. Graphite has a low absorption coefficient for X-rays and neutrons, which are important properties in nuclear applications. It also has a low coefficient of friction. All these properties make the metallurgical and lubricant industries the main end-users of graphite, and these sectors together consume about 60-70 % of the world production (European Commission, 2020).

Graphite production requires extensive mineral processing, which normally involves crushing, milling and flotation, and re-milling in several steps, with or without a final chemical purification. It is the quality and properties of the final graphite concentrate that determines the end-use and price.

The discovery of the unique physical properties of the 2-dimensional carbon layer (graphene) and the subsequent Nobel prize in physics for 2010 (http://www.nobelprize.org/nobel_prizes/physics/laureates/2010/index.html), led to a large increase in the exploration for new graphite deposits worldwide. A large number of new patents and new and revolutionary applications have been suggested. However, as of today few single end-uses of graphene have come into production, that also, on the short term, need natural graphite to such an extent that it drastically will increase the need for natural graphite. It is therefore uncertain to what extent new applications that use graphene will affect the market for natural graphite.

The end use for the applications that is the aim of this work package is the rechargeable Li-ion batteries. This end-use requires a graphite product that contains > 99 % C, a grade which is usually only obtainable after chemical purification of a standard graphite concentrate in excess of 95% C. In addition, the graphite for batteries needs to be modified to a spherical particle shape; a

process with low recovery, and about 3 tons of flake graphite is needed to produce 1 ton of spherical graphite. In addition, the graphite spheres have to be coated. The coating material can consist of carbon, or a combination of different metals, such as lithium, titanium or silicon. The purpose of the coating is to create an ideal energy barrier between the graphite spheres in the anode material. It is expected that growth in the use of rechargeable batteries will be the main driver for increased graphite consumption in the future. (Yoshio et al., 2003; Yoshio et al., 2004).

Traditionally graphite concentrates are classified and sold according to flake size and in classes shown in Table 6.

Powder/fine flake	Carbon content
Max 20% > 75 micron	> 85%
Medium flake	
Max 20% > 150 micron	
Max 20% < 75 micron	> 92 %
Coarse flake	
Max 80% > 150 micron	> 92 %

Table 6 Traditional trade products of graphite

The market price for the finished product depends mainly on the flake size and carbon content. Highest price (about 800 US\$ per ton) is paid for the +150-micron size fraction with carbon content of 94-97%. For the same size fraction but carbon of 85-87% the market price is about US\$ 340 per ton (www.indmin.com accessed 02.12.2020). Spherical and chemically purified graphite with a carbon content of > 99% that are tailor made for particular end users can reach prices > US\$ 10.000, - per ton, but these products are traded between producer and end user and the price picture is not transparent for others. Most graphite producers have a large variation of products tailored to specific customers. Grain size distribution and total carbon content of the finished products are the main variables.

In analyses of graphite bearing rock the industry commonly uses the term "carbon graphitic" (Cg) this is a parameter that is essentially the same as total organic carbon (TOC) but includes an initial step where organic matter is roasted off before removal of carbonate minerals and subsequent carbon analysis. In rocks without any organic matter or carbonates analysis of total carbon (TC) would be equal to Cg and TC analysis is much cheaper and faster to do.

5.2 Field relationships of graphite deposits

Since graphite most commonly is of biological origin, it usually occurs in metasedimentary rocks often associated with rocks such as quartzites, arkoses and carbonates, and since graphite occurrences usually are formed as a result of high grade metamorphism they host rock usually metamorphosed and recrystallised so that there are little traces of the primary sedimentary rocks. In addition, comes the fact that graphite bearing rocks most commonly is the most weathered and poorly exposed rock unit everywhere they occur. The field relationships flake graphite occurrences are described e.g., by (Baiju et al., 2005; Gautneb et al., 2020; Gautneb & Tveten, 1992; Palosaari et al., 2016; Palosaari et al., 2020) and typical geological setting and associated country rocks is shown in Figure 14.

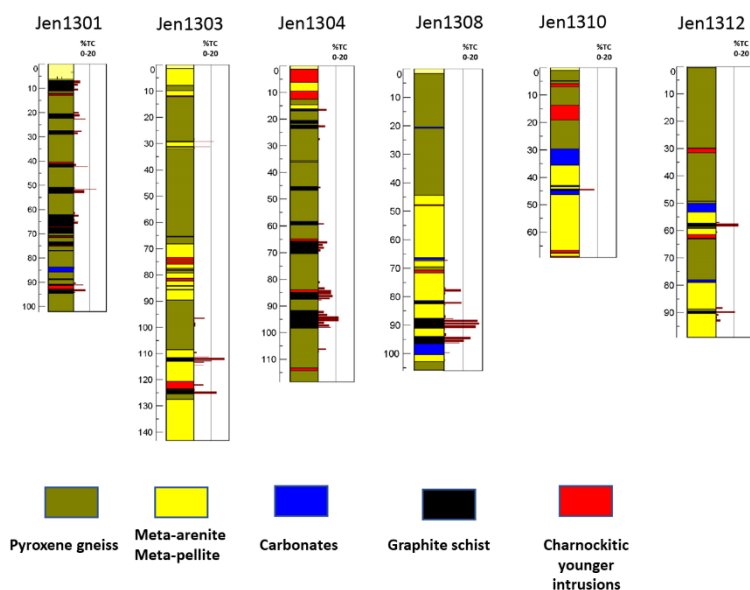


Figure 14 Drill logs showing the typical distribution of graphite rich layers and associated country rock types (from Gautneb et al 2020)

Vein type of graphite usually occurs as thin veins in high grade gneissic rocks. The width of veins can vary widely but are most commonly in economic deposits in the order of some tenths of centimetres. There are few vein type occurrences that are regarded to have an economical potential in Europe today and the reader is referred to e.g. (Rumble, 2014; Touret et al., 2019) and references therein for their general description.

Amorphous graphite is, as described above microcrystalline variety of flake graphite, usually formed at lower metamorphic facies and commonly also with contact metamorphism, apart from these relationships the geology of amorphous graphite is similar to that of flake graphite.

5.3 Exploration for graphite deposits

Since at all localities graphite, graphite bearing schists, are the most weathered and overburden rock, indirect (geophysical) methods are almost always used to find and delimit graphite occurrences. Since graphite is a very good electrical conductor electromagnetic (EM) and electric methods. The interested reader should consult general textbooks e.g. (Dentith & Mudge, 2014) for a general description of these methods. The approach used everywhere is almost the same, depending on level an exploration program starts. First the work typically starts with regional geophysical investigations (usually airborne), this is followed up with local ground geophysics and geological fieldwork. If potential targets are located the core drilling and metallurgical test usually follows. This part of such approach is illustrated in Figure 15 A-C.

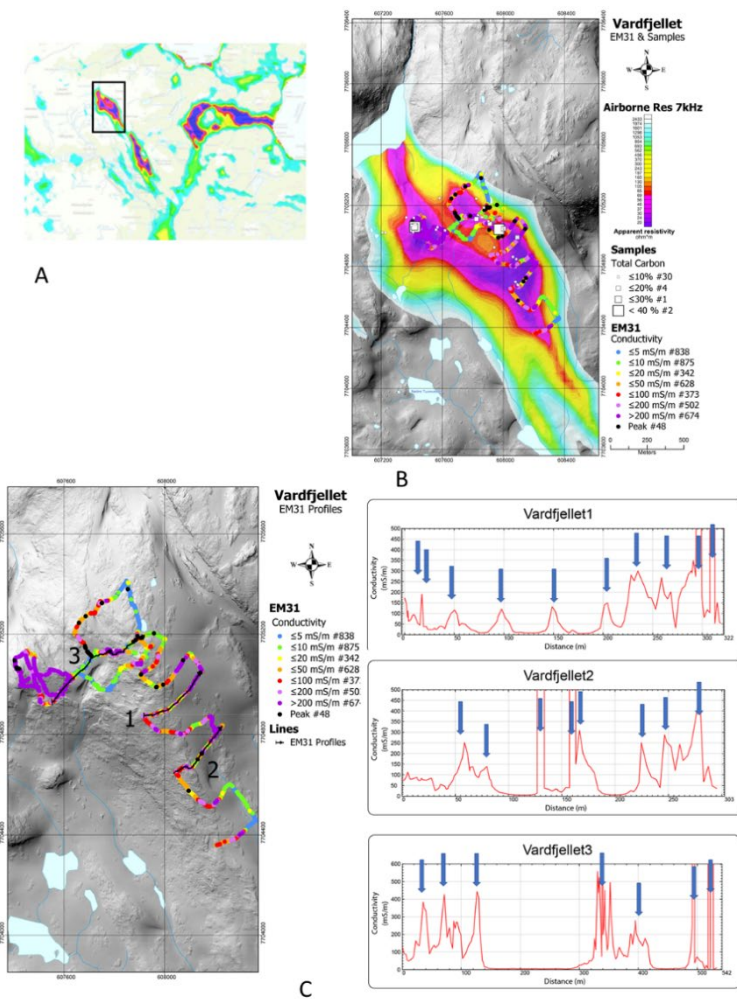


Figure 15 Figures showing the some of the steps in graphite exploration a) airborne geophysics b) and c) ground geophysics. Blue arrows show indicate graphite lenses along profile 1-3. From (Gautneb et al., 2020).

Figure 15a shows large scale aero geophysical map where several areas where electrical conducting rocks are apparent. Figure 15b show a zoom in one of these areas with superimposed ground geophysical EM measurement Figure 15c shows the ground geophysics only, three traverses are shown to the right. The blue arrows indicate lenses of graphite schist that. What is apparently a homogenous mineralisation from airborne measurements is quite complex in details. (Gautneb et al., 2020). A similar approach, that also include metallurgical testing of the graphite concentrate for its battery properties is described by (Al-Ani et al., 2020).

6 Summary and conclusions

In Europe the lithium cobalt and graphite occurrences occur in many geological settings. Lithium cobalt and graphite are also produced either directly or indirectly from several deposits. Reports give a summary of the different geological settings in which these commodities occur in Europe.

Lithium

There are about 120 different lithium bearing minerals, 12 of these are the most common and, of these, spodumene (containing 8.03 wt.% Li_2O) is the most common. The following types of Lithium occurrences are described in this report:

Lithium cesium tantalum (LCT) pegmatites; Several models are proposed in the literature for the formation of these types of mineralisation and we give a review of the granitic source and partial melting model, and both require strict geological setting and processes to occur. Compared to the common nature of pegmatites in general, lithium bearing pegmatites must be regarded as rare. Typical deposits of this type in EU are: Spodumene-bearing pegmatites from the Kaustinen province (Finland), from the Barroso-Alvão pegmatite field (Portugal), from the Lalín-Forcarei pegmatite field (Spain) and from the Eastern Alps (Austria).

Li-rich Rare metal granites; Rare metal granites are peraluminous granites that are enriched in various types of metals. They are believed to be produced by melting of sedimentary rocks. They can contain from 0.5-1.0 % Li_2O . The lithium bearing minerals are typically phosphates and phyllosilicates. The rare metal granites usually represent much larger volumes when compared to pegmatites. Typical deposits of this type in EU are encountered in the rare-metal granite belt of the French Massif central (Beauvoir, Montebbras, Richemont) and in Portugal (Argemela).

Greisen; Greisen are hydrothermally altered rocks that are associated with granitic intrusions. Lithium-rich greisen are generally developed within rare-metal granite. Typical Li_2O grades are about 0.4%. The composition of the granitic precursor seems to be important for the enrichment of Lithium in the associated greisen. Large Lithium-rich greisens are located along the Czech-German border (Cinovec, Zinnwald, Sadisdorf, Krásno).

Lithium phosphate quartz veins; In the final stage of crystallization of rare metal granites, fluids rich in silica, phosphorous, lithium and fluorine can be formed. The Argemela mine deposit in Portugal is the present-day best known example. Other occurrences are known in Portugal and France (Montebbras).

Stratiform sedimentary-hydrothermal lithium mineralisation; This type of deposits represents localities where there have been a flux of lithium bearing fluids over a long period of time. Usually some form of depression or sedimentary basin are the traps for lithiums in these types of occurrences. These types of occurrences have the following sub types:

Clay-type: Several clay minerals can be lithium bearing, the weathering conditions and host rock compositions determine the clay mineral composition and its lithium content. Typical lithium contents are 2000-3000 ppm. EU Potential for this type of deposit should be significant but has never been assessed.

Brines: Brines are defined as hypersaline solutions with 1.7 to 2x times that of seawater. They can be related to geothermal processes or non geothermal. Lithium brine occurrences tend to be very large and usually form large salt type deposits (salars). Typical lithium contents are in the order < 350 ppm/L. Geothermal Lithium-rich brines are outside the focus of this study but

several significant mineralisation is known in upper Rhine valley (France and Germany), in Italy and in Cornwall (England).

Jadar type: The jadar type of Lithium occurrences is regarded as a “non-conventional” lithium occurrence. The occurrence formed in the Lopare basin of NW Serbia and is hosted in 400-500 thick succession comprising clay- silt- and sandstone. The formation of the mineral Jadarite ($\text{LiNaSiB}_3\text{O}_7(\text{OH})$) is poorly understood. If an economical mineral processing of jadarite is developed by Rio Tinto, the Jadar deposit will be a world-class deposit around 2025.

Lithium bearing bauxites: bauxites can contain variable content of lithium minerals such as Li-bearing clays and Li-manganese oxides. In China Lithium content up to 0.53% Li_2O are found. Some lithium-bearing bauxites are known in Hungary and Greece. EU Potential for this type of deposit should be significant but has never been assessed.

Non economic Lithium mineralisations : Mn(Fe) deposits; These deposits which are normally explored for their Mn and Fe content can contain small amount of the lithium bearing mineral lithiophorite, however in so low content that this deposit type is uneconomic. **Aalenian black shales:** In the Dauphiné region of France lithium levels of around 400 ppm are reported occurring in tension cracks and disseminated in the shale. Lithium enrichment are very local and non-economical.

Cobalt

Pure cobalt does not occur in the nature but cobalt is an element in about 25 minerals. In geological context cobalt behave very similar to nickel and most occurrences of nickel represent occurrences also of cobalt. Very commonly nickel smelters produce a nickel matte which are refined to produce nickel cobber cobalt and PGE metals. It is very rare to find cobalt as the main product of a deposit. The following genetic types of Cobalt occurrences are described in this report:

Magmatic Ni-Cu-Co deposits: In these types of deposits cobalt occur in the minerals such as pentlandite ($(\text{Ni,Fe})_9\text{S}_8$) with a typical content from 0.5-3% and in pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$) with a normal content of 0.05-0.2% Co. In general, the nickel content of these deposits determines the cobalt content. Typical deposits of this type in Europe are mafic-ultramafic rock –hosted deposits in Fennoscandia (Finland, Norway and Sweden) with a few rare occurrences elsewhere.

Sediment hosted Cu-Co deposits: These are the most important sources for cobalt with about 64% of the world's production. Their general setting is in intracratonic sedimentary basins. Typical levels of Cu and Co are in the range 1-5% and 0.01-1-1% respectively. In the Katanga province DRC several large deposits are located with cobalt levels of more than 0.5%. The Kupferschiefer deposits of Poland and Germany are examples of Cu-deposits of this type but they typically contain very low Co contents.

Vein type deposits (5 element vein deposit): These deposits represent hydrothermal deposits where the metals were deposited from hyper saline solutions (>20% NaCl). They typically contain a number of different elements such as silver bismuth, cobalt, nickel and arsenic. A number of the historical mines in central Europe (Germany, France, Austria, Slovakia, Italy and Spain) are of this type.

Sea floor hydrothermal system (Cu-Zn-Pb VMS deposits): This type deposits are among the world's most important copper, zinc, and lead and not uncommonly economical levels and of gold and silver. Cobalt levels are usually >100 ppm and can in some cases reach up to 0.2-0.4%. Cobalt-bearing minerals are pyrite, pyrothite and Co-pentlandite. The Cu-Zn-Co-Ni deposits of the Outokumpu region in Finland are known for their high Co-contents (0.1-0.25 %) and also produced cobalt in the past.

Lateritic Ni-Co deposits: These deposits are related MgO-rich ultramafic rocks of various origins. The primary rock is already enriched in Ni and Co and the weathered laterite contains typically about 1% of Nickel and 0.01-0.2% Cobalt. Worldwide they represent an important deposit type for Ni and Co. In Europe there are a number of these occurrences on the Balkan peninsula, some of which have been mined for Ni but cobalt was not utilized.

Graphite

The scientific community uses a different approach of classification of carbonaceous material compared to the industry. Somewhat simplified one can say that the academia uses the crystallographic properties of the carbonaceous material for their classification, while the industry uses the grain size and grain properties of the graphite for their classification. The genetic type of graphite using the industrial approach is:

Flake graphite: Flake graphite is graphite formed in metasedimentary rocks of high metamorphic grade. These deposits are characterized by the presence of flakes of individual graphite crystals in variable grain size.

Amorphous graphite: The term amorphous graphite is misleading, microcrystalline graphite is a more correct description. This type of graphite is formed most commonly from coal deposits altered by contact metamorphism, or from low metamorphic (up to mid greenschist facies) grade organic-rich shales.

Vein or lump graphite: This is a special type of graphite deposit that currently only are mined in Sri Lanka. They are formed by processes that involve the interaction of CO₂, CO, CH₄ and H₂O during metamorphism, subsequent deposition of the carbon from hydrothermal solutions although mined only on Sri Lanka their geological occurrences worldwide are more common.

In Europe the graphite mines in Norway and Ukraine are of flake type and in Austria of amorphous type.

Compared to the occurrences of lithium and cobalt, there is a larger proportion of the graphite occurrences that are unclassified for their genetic type. The reason for this is that geological studies of graphite deposits are much less frequent than studies on other commodities.

We believe that the potential for new discoveries of lithium, cobalt, and graphite are large in many areas. As is shown in our WP5 deliverables the occurrences show a strong clustering and are outlining areas where geological processes have favored formation of these materials. It is important that the geological surveys continue their cooperation to systemise their national occurrence database and harmonize them on a European basis.

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8 Appendix 1, Overview of partners, contributors, the collected data and its organisation.

Table 7 List of Partners/countries, MREG members and individuals that delivered data to WP5.

Institution	Country	
Project partners		
CGS	Czech Republic	
GTK	Finland	
BRGM	France	
GSI	Ireland	
NGU	Norway	
LNEG	Portugal	
IGR	Romania	
GeoZs	Slovenia	
IGME	Spain	
SGU	Sweden	
GeolInform	Ukraine	
MEREG members*		
BGS	Great Britain	
BGR	Germany	
PGI-NRI	Poland	
	Slovakia	
RBINS	Belgium	Data from B. Gourcerol
	Bosnia-Herzegovina	Data from BRGM
	Serbia	Data from BRGM
HGI-CGS	Croatia	
IGMEgr	Greece	
IGR	Romania	
	Switzerland	Data from BRGM
ISPRA	Italy	
Individual contributors		
Manuel Scharrer	Germany	Univ of Tübingen
Stefan Horn	Great Britain	BGS
Blandine Gourcerol	France	BRGM

* Mineral resources expert group of the Eurogeoseveys.

The following information was requested from the partners and other data suppliers (Table 2).

Table 8 Data requested for the occurrences of Li, Co and graphite in Europe.

Data field	Field values		
Id			
Deposit name			
Country name			
Element	Li, cobalt, graphite		
Genetic type	See table 3		
Genetic sub type	See table 3	Only for Li	
Latitude	Decimal degrees		
Longitude	Decimal degrees		
Status	Active, closed, not exploited, Active, no Co production*.		
Occurrence's type**	Occurrence, Prospect, Deposit Mine Tailing		

* This term is used for active mines, that produce a companion element usually Ni, but where Co presently is not a by-product.

** Here we follow the INSPIRE definitions which in a simplified form can be defined as:

- a) Occurrence: Locality with an enrichment of a component above normal values.
- b) Deposit: Locality with an enrichment of a component above normal values, that also usually has a grade and tonnage estimated. This estimation can be compliant with international standards like PERC, JORC or UNFC, or noncompliant. The grade and tonnage information can be confidential.
- c) Prospect: Locality with an enrichment of a component above normal values, that lack the grade and tonnage estimate, but have a defined areal extent.
- d) Mine tailing represents an anthropogenic locality that can be occurrence or deposit.

Many elements occur as accompanying elements and are only produced as a by-product when there is production of the main elements. Many elements are also enriched in nature by different geological processes, creating a large number of complex genetic types and ore forming processes. This is particularly the case for lithium and cobalt. For Co we regard any deposit with more than 100 ppm Co as a potential resource. This cut-off value was used with some difference between the various partners. In Norway for instance this cut-off was set to 300 ppm Co, to exclude a number of minor occurrences, taking care that that clusters remain to define prospective areas.

All together our database consists of 1624 occurrences/deposits that are distributed in the European countries as shown in Table 4.

Table 9 The number of occurrences per country and element.

Country/element	N	Country/element	N
Albania	9	Norway	159
Co	9	Co	85
Austria	298	Graphite	59
Co	16	Li	15
Graphite	232	Poland	43
Li	50	Co	32
Belgium	8	Li	11
Li	8	Portugal	209
Bosnia and Herzegovina	3	Graphite	4
Co	2	Li	205
Li	1	Romania	28
Czech Republic	67	Co	13
Co	4	Graphite	10
Graphite	31	Li	5
Li	32	Serbia	13
Finland	166	Co	5
Co	123	Li	8
Graphite	11	Slovakia	13
Li	32	Co	6
France	76	Graphite	1
Co	18	Li	6
Graphite	15	Slovenia	3
Li	43	Graphite	2
Germany	21	Li	1
Graphite	1	Spain	131
Li	20	Co	34
Greece	11	Graphite	30
Co	5	Li	67
Graphite	2	Sweden	166
Li	4	Co	63
Greenland	82	Graphite	75
Co	70	Li	28
Graphite	9	Switzerland	2
Li	3	Li	2
Hungary	8	Ukraine	64
Li	8	Co	16
Ireland	11	Graphite	35
Co	1	Li	13
Li	10	United Kingdom	29
Italy	21	Co	18
Co	4	Li	11
Graphite	3	Grand Total	1624
Li	14		
Kosovo	2		
Co	2		
North Macedonia	5		
Co	4		
Li	1		

Appendix 2 Maps of Lithium cobalt and graphite occurrences.

