

CHEMICAL-MINERALOGICAL CHARACTERIZATION OF CARBONATE-CLAY TYPE LITHIUM ORE

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Abstract

The need for lithium minerals has surged significantly in recent years due to their use in lithium compounds for lithium-ion batteries, portable electronic devices, and energy storage systems. Spodumene is the primary lithium-containing mineral being explored and processed today because of its high lithium concentration and the widespread availability of deposits. However, other types of ores containing minerals such as lepidolite, petalite, zinnwaldite and hectorite are becoming increasingly important. This paper presents the characterization of carbonate-clay ore type, in which an increased lithium and boron content was determined – 1010 ppm and 4351 ppm respectively. Based on the findings, lithium is mainly associated with clay minerals such as smectite and illite, while boron commonly exists in the minerals probertite and sirlesite. The ore originates from a previously unexamined deposit from the European territory. Petrological analyses have determined that the ore sample lies at the border of fine-grained carbonate clastite and low carbonate marl.

Keywords: Clay-carbonate lithium ore, Chemical composition, Mineralogical composition

1. INTRODUCTION

Due to its role in the production of electric cars, lithium has become a valuable resource worldwide. The need for highly efficient lithium compounds is expected to grow exponentially in response to the growing demand for electric vehicles and other strategic lithium-based technologies [1]. This is in line with the goals of the climate-neutral European Union until 2050, which is why there is an increasing demand for new sources of domestic lithium raw materials. It is believed that by 2040, up to 90% of the need for lithium will exist precisely because of its key role in the production of batteries, which is a crucial factor for environmentally friendly technologies [2]. As there is currently no viable alternative to lithium-ion batteries, the use of lithium in the market is growing faster than other essential materials used in batteries: for example, some electric vehicle batteries can function without one or two common components, such as Ni, Co, Mn or graphite, but not without Li [3]. In accordance with the above, and taking into account the criticality of lithium as a raw material, it is necessary to adjust the national production base of the countries of the European Union, in order to meet the growing demand for certain forms of lithium, such as lithium carbonate. Therefore, the expansion of lithium ore production in the EU is necessary in order to increase domestic supplies in the lithium market [4]. However, lithium deposits in the EU are associated with different mineralizations in solid host rocks, which require a special approach during processing and refining to achieve lithium carbonate of suitable battery quality. Spodumene from pegmatite deposits is expected to be the main source of lithium from ores at present, although future sources would most probably include other minerals such as

lepidolite, petalite, zinnwaldite, jadarite and hectorite [1]. Physico-chemical and mineralogical characterization of lithium ore of the clay-carbonate type is given in the paper.

2. EXPERIMENTAL

2.1 Sample preparation

Lithium-bearing ore sample was homogenized by multiple application of the cone-ring methodology, and after homogenization, shortening of the sample was performed by quartering and reduction on the Jones riffle splitter (Figure 1). A chessboard method was used for taking the representative samples for physico-chemical and mineralogical analyzes (see Figure 2).



Figure 1. Shortening of the sample on the Jones riffle splitter



Figure 2. Taking the representative samples by chessboard method for

2.2 Physical characteristics

Density of the tested sample is 2,494 t/m³, while the bulk mass in the loose and compacted state is 1333.30 kg/m³ and 1566.90 kg/m³, respectively. The Bond work index in the rod and ball mills is 16.06 kWh/t and 10.38 kWh/t, respectively, and the natural pH is 9. The sample is very fine-grained, and was later found to be very suitable for lithium extraction by the bioleaching process.

2.3 Chemical composition of sample

Chemical analysis of the sample was performed at the Mining and Metallurgy Institute Bor. The results of chemical analysis are presented in Table 1 i Table 2.

Table 1. Chemical composition of lithium-bearing ore sample (macro components)

Content, %							
SiO ₂	Al ₂ O ₃	CaO	K ₂ O	Fe ₂ O ₃	Na ₂ O	MgO	P ₂ O ₅
29.78	7.44	18.32	4.07	3.73	2.21	9.82	0.055
MnO	TiO ₂	LOI	Org. C	O.M.	V ₂ O ₅	Cr ₂ O ₃	/
0.085	0.23	23.02	<0.05	<0.10	0.011	0.017	/

Table 2. Chemical composition of lithium-bearing ore sample (micro components)

Content, mg/kg								
Li	B	Sr	Cd	As	Hg	Ba	Be	Bi
1010.5	4351	2482.2	0.19	16.5	0.1	464.2	1.7	<1.0
Co	Ga	Ge	Hf	Nb	Ta	W	Ni	Sc
11.1	11.9	<5.0	1.2	6.3	<1.0	1.3	81.2	8.9
Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
10.2	15.5	35.7	4.1	15.1	3	0.64	2.4	0.37
Dy	Ho	Er	Tm	Yb	Lu	Th	U	/
2	0.39	1.1	0.15	1.1	0.15	6.6	2.6	/

Based on the results of the chemical analysis, it was determined that the average lithium content in the sample is 1010.5 ppm, while the boron content is 4351 ppm. The samples show a relatively high content of SiO₂, Al₂O₃, CaO and MgO (29.78%, 7.44%, 18.32% and 9.82%, respectively), as well as a significant value of loss on ignition (23.02%), which indicates the significant presence of aluminosilicates and silicates, as well as typical carbonate minerals (calcite, magnesite/dolomite) in the samples.

2.4 Mineralogical composition of sample - X-ray method

Phase composition of the sample. The X-ray powder diagram (diffractogram) of the investigated sample is given in Figure 3. The database search revealed that the following minerals are present in the sample: **probertite**, $\text{NaCaB}_5\text{O}_7(\text{OH})_4 \cdot 3\text{H}_2\text{O}$, **calcite**, CaCO_3 , **dolomite**, $\text{CaMg}(\text{CO}_3)_2$, a mineral from the **potassium feldspar** group, KAlSi_3O_8 , a mineral from the **plagioclase** group, $(\text{Na,Ca})(\text{Si,Al})_4\text{O}_8$, **analcime**, $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ and **searlesite**, $\text{NaBSi}_2\text{O}_5(\text{OH})$. A significant presence of minerals from the group of layered silicates was also observed, which were indirectly identified using X-ray diffractograms of oriented preparations. The diffraction peak at $26.70^\circ 2\theta$ ($d \sim 3.34 \text{ \AA}$) indicates the possible presence of quartz.

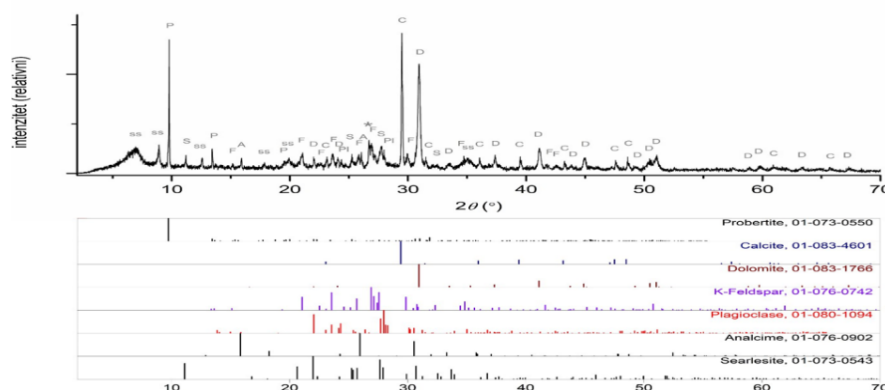


Figure 3. X-ray diffractogram of sample with reflections of identified phases. Peak legend: P – probertite, C – calcite, D – dolomite, F – K-feldspar, Pl – plagioclase, A – analcime, S – searlesite, ss – minerals from the layered silicate group.

Figure 4 shows X-ray diffractograms of oriented preparations made from the sample. Using them, the following clay minerals were identified: minerals from the **smectite** group, minerals from the **illite** group and minerals from the **chlorite** group.

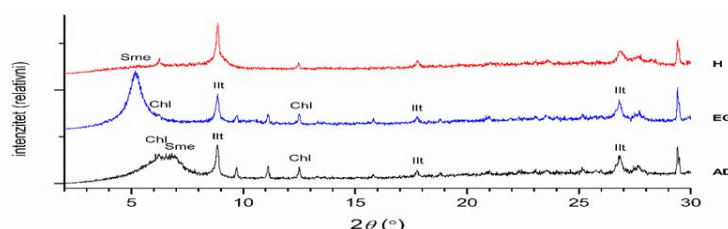


Figure 4. X-ray diffractograms of oriented "composite" sample preparations with identified minerals from the layered silicate group. Legend: Sme – smectite, Ill – illite, Chl – chlorite; AD – oriented untreated, EG – saturated with ethylene glycol, H – annealed for 1h at 550°C .

The proportion of individual crystalline phases in the samples identified by the WPPF method ("whole-powder-pattern fitting") using PDXL 2.8.4.0 software. (Rigaku, 2007) given in Table 2.

Table 2. Phase composition of the tested samples.

Phase	dolomite	calcite	K-feldspar	plagioclase	probertite	searlesite	analcime	smectite	illite	chlorite
Mass share	23	15	16	3	14	5	1	9	11	3

In addition to the identification of the minerals present, emphasis was placed on the determination of the minerals carrying the chemical element lithium. The results of the X-ray diffraction method on polycrystalline material (PXRD method) did not identify minerals that contain lithium in their chemical composition. However, based on the chemical analysis (Table 1), an increased content of lithium is observed. The presence of lithium is probably related to clay minerals (minerals from the layered silicate group). Lithium mineralizations in smectite clays are known (primarily the mineral hectorite $\text{Na}_{0.3}(\text{Mg,Li})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ – the so-called hectorite deposits), while mineralization in illite-type clays has also been mentioned recently.

2.5 Petrological analysis

Macroscopic appearance of the rock. The rock is light gray with brown tones. According to the reaction to HCl, the rock is at the border of carbonate fine-grained clastite and low carbonate marl. If the brown color is more pronounced, then the laminae in those sets have more carbonate components. According to the sample, the rock is thinly layered where each layer over 1 cm thick represents a set or coset. The sets of laminae are slightly deformed. Rare white, slightly wavy laminae were also observed, which may be tuffaceous. Flaky forms are present in the rock (Fig. 5) and small individual irregular grains of sulphide.

Microscopic appearance of rock. The rock is laminated, the sets are built from laminae that differ from each other in terms of carbonate content, i.e. clay minerals. Therefore, the rock is a mixture of dolomicrite and fine-grained clastites (Fig. 6). Certain deformed laminae have a high content of sulfide flakes and may be primarily tuffaceous, which was observed macroscopically. Definition of the rock: **dolomitic marl**.

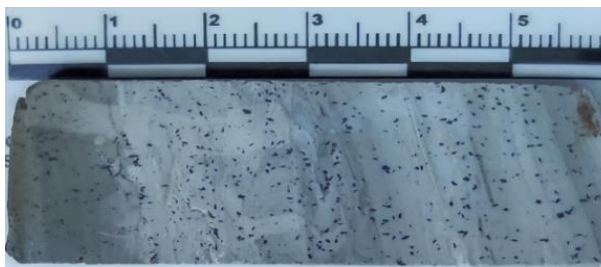


Figure 5. Macroscopic appearance of sample



Figure 6. Laminated dolomite marl. XPL.

3. CONCLUSION

Characterization of lithium-bearing ore is performed regarding chemical and mineralogical-petrological composition. This type of ore contain increased amount of lithium (1010 ppm), as well as boron (4351 ppm). According to the mineralogical X-ray analysis, lithium is primarily bound to clay minerals of the smectite and illite type, while boron is predominantly present in the form of the minerals probertite and sirlesite. Petrological tests have shown that this type of ore belongs to dolomitic marls.

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