

Study on REE occurrence in a Svanbergite and basic ore characteristics

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Abstract: Svanbergite in Sichuan Province, China is a special middle-low grade phosphorus ore. It contains rare earth elements (REEs), aluminum, and strontium that can be exploited and utilized. In this study, several methods were used to systematically study the occurrence of REEs in the ore and basic ore characteristics. The ore, which was rich in REEs, Al, and Sr, was classified as marine sedimentary low-grade phosphorus ore. The main ore mineral was crandallite and pyrite, and independent REE minerals were not found. Crandallite was the main carrier mineral of useful elements, including P, REEs, Al, and Sr. REE³⁺ was inferred to mainly exist in crandallite via isomorphism by replacing Ca²⁺ and H⁺. The crandallite was mainly characterized as fine-grained, and minerals were closely disseminated. The results from this study will provide a valuable reference for expanding available REE resources and the efficient comprehensive utilization of svanbergite.

Keywords: svanbergite, rare earth elements (REEs), occurrence state, crandallite, ore characteristics

1. Introduction

Devonian Shifang-type phosphorus ore is a marine sedimentary phosphorite deposit discovered in central and western Sichuan. Svanbergite layer was first discovered in this deposit, mineral body with lenticular style is the direct roof of phosphatic rock. The ore belt mainly lies at Mianzhu and Shifang, Sichuan Province (Duan et al., 1964; Sun, 1966; Wang and Li, 1988; Li, 2018).

Svanbergite is a special kind of aluminum phosphate ore, which is a rare comprehensive deposit at home and abroad with mainly phosphorus, accompanied by sulfur, aluminum, strontium, rare earth, and other elements. among which the content of rare earth elements is more than twice total rare-earth content ($251.1 \times 10^{-6} \sim 974.15 \times 10^{-6}$) of the Xinhua REE-bearing dolomitic phosphatic rock, Zhijin county, Guizhou Province (Zhang et al., 2008). Due to the complex chemical composition, it is difficult to achieve element separation, and it is still in the stage of use as fertilizer after roasting (Wang et al., 1986; Wang and Xia, 1994; Wang and Jin, 1995). However, with the increasing demand for rare earth elements worldwide, rare earth elements in svanbergite will become an important potential resource. And the comprehensive utilization of rare earth elements in the ore can greatly improve the development value of the ore.

Since the '80s, many researchers have done a lot of researches on the ore comprehensive utilization. Such as preparing phosphate fertilizer and phosphoric acid after roasting (Wang and Xia, 1991; Song and Wang, 1994; Zhang et al., 2007; Yu et al., 2008), recovering pyrite by flotation (Wang, 1978; Tang, 1898), refining yellow phosphorus by electrothermal method, extracting aluminum, and recovering strontium and rare earth (Huang, 1977), making strontium salt, aluminum chloride and aluminum dihydrogen phosphate after hydrochloric acid decomposition (Huang, 1985) etc. However, a detailed

study on the status of rare earth in svanbergite has not yet been presented or published. In this context, this study aimed to provide a valuable reference for the development and utilization of the available rare earth elements resources.

2. Materials and methods

2.1. Materials

Wangjiaping phosphate ore is the representative deposit of Shifang-type phosphate deposit, the svanbergite reserves are about 60 Tg (Tang, 1978). Dengjiahuodi mine section (E: 104°01'52" - 104°03'45", N: 31°29'23" - 31°31'02") is one of the mining areas, it is surrounded by mountains and dense vegetation (Fig. 1 (a)). From top to bottom, the phosphate-bearing strata of the deposit are as follows: phosphorous clay rock, svanbergite, and phosphorous rock strata. Svanbergite is the direct roof of the phosphate rock strata, and pyrite is oxidized to limonite on the surface of the ore. The strata stratigraphically above and below the phosphorus-bearing strata are dolomite.

In this study, the ore samples were collected by grid method from the fresh surfaces of the svanbergite ore bed in this mine section. As shown in Fig. 1(b), the colour of the ore is mainly grey, showing a dense massive structure. The ore samples were crushed in a jaw crusher (PEX-100×100, Guiyang Mine Exploration Machinery Plant), the crushed product was reduced and then ground by a disc crusher (XPF-Φ150B, Guiyang Mine Exploration Machinery Plant) to produce -75 μm sample for the chemical analysis and chemical phase analysis. Additionally, thin sections of the representative massive ore samples were prepared for AMICS analysis.

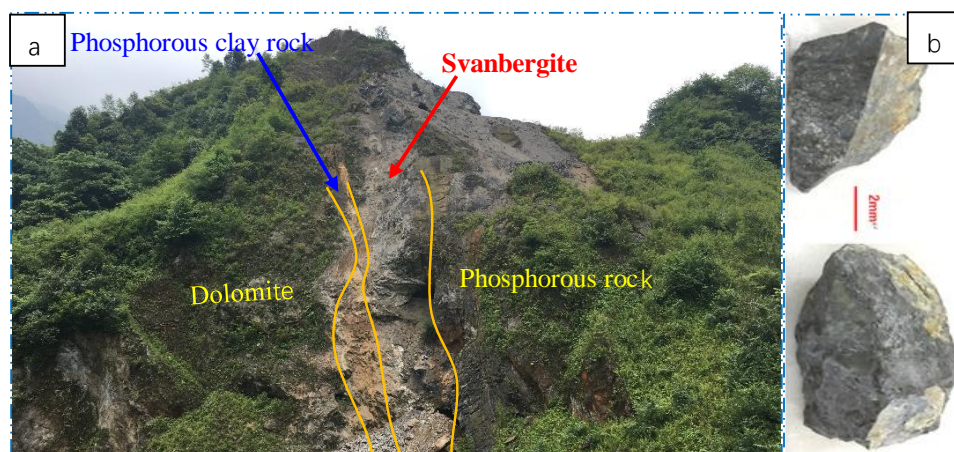


Fig. 1. (a) Wangjiaping phosphate-bearing strata of the deposit, (b) Svanbergite ore

2.2. Methods

2.2.1. Chemical composition analysis

The content of major element oxides in the ore was determined by X-ray fluorescence spectrometry (P61-XRF26s). The contents of trace elements and rare earth elements in the ore were determined by melting inductively coupled plasma mass spectrometry (ME-MS81). Both tests were completed by Aoshi Analysis and Detection (Guangzhou) Co., Ltd.

2.2.2. Mineral composition and characteristics analysis

An automatic mineral identification and characterization system (AMICS) (SEM: Sigma 300, Zeiss, Germany; Energy spectrometer: Quantax 400, Brook, Germany; Mineral analysis software, Brook, Germany) was used to quantitatively analyse the mineral characteristic parameters of svanbergite, and the tests were completed with a compass test platform. The hardware of the AMICS consists of a Zeiss scanning electron microscope (Sigma 300) and Brooke energy spectrometer (Quantax 400), and the software consists of Brooke AMICS mineral analysis software. The scanning electron microscope test

parameters were as follows: voltage: 20 kV, working distance: 8.65 μm , scanning accuracy: 2.79 μm , and scanning area: 10 mm \times 10 mm.

2.2.3. Chemical phase analysis

Based on the mineral composition analysis results of AMICS, the main minerals of svanbergite (apatite, pyrite, and crandallite) were selected as the main carrier mineral phase of rare earth elements in the chemical phase analysis. In addition to this, it was necessary to analyse the ion adsorption phase of rare earth elements. According to the relevant research results (Zhang, 1992; Gong, 1996; 2007; Ding et al., 2017), the experimental steps of chemical phase analysis were established as shown in Fig. 2.

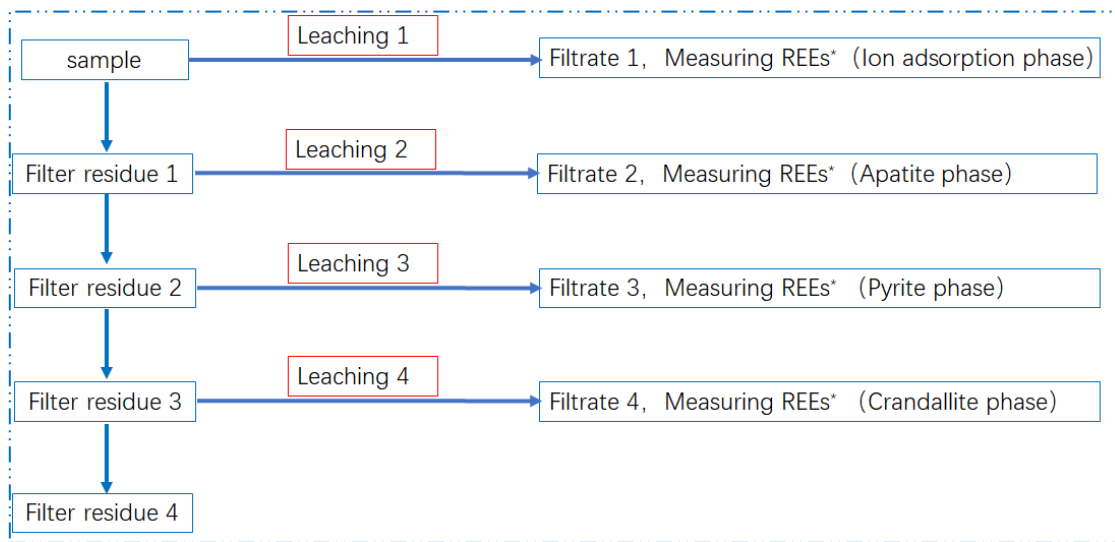


Fig. 2. Chemical phase analysis process of rare earth elements

Because the ore is rich in LREEs and the rare earth element yttrium and the contents of La, Ce, and Y account for 67% of the total content of REEs, the term REEs* is selected to represent the content of REEs in each phase for testing and analysis. An inductively coupled plasma spectrometer (ICP-AES) was used to measure REEs* in each phase. The water used in the experiment was prepared by ultrapure water system (TST, Shijiazhuang Tester Instrument Co., Ltd). The detailed operations and conditions of the chemical phase analysis of rare earth elements are as follows:

Leaching 1: -75 μm , 1 g samples, and 100 cm³ of 30 g/dm³ (NH₄)₂SO₄ ((NH₄)₂SO₄, AR, Chengdu Jinshan Chemical Reagent Co., Ltd) solution were put into a beaker, and after a water bath (Digital Thermostat Water Bath, HH-4, Changzhou Zhiboorui Instrument Manufacturing Co., Ltd) for 1 h with stirring (Motor agitator, JJ-1A, Jintan Xinrui Instrument Factory) at room temperature (25°C), the filtration was performed. Filtrate 1 was analysed for REEs* based on ionic adsorption, and the filter residue 1 was reserved for the measurement in the next phase.

Leaching 2: Filter residue 1 was transferred to a beaker, 200 cm³ of 20 g/dm³ malic acid (C₄H₆O₅, AR, Tianjin Dingshengxin Chemical Co., Ltd) solution was added to a water bath for 30 min with stirring at room temperature (25°C), and the filtration was performed. Filtrate 2 was analysed for REEs* in the apatite phase, and the filter residue 2 was reserved for measurement in the next phase.

Leaching 3: Filter residue 2 was placed into a beaker, 150 cm³ of saturated bromine water (Br₂, AR, Chengdu Jinshan Chemical Reagent Co., Ltd) and 0.15 g of potassium dichromate (K₂Cr₂O₇, AR, Chongqing Maoye Chemical Reagent Co., Ltd) were added, and the filtration was performed after a water bath for 1 h with stirring at room temperature (25°C). Filtrate 3 was used to analyse the REEs* in the pyrite phase, and the filter residue 3 was reserved for measurement in the next phase.

Leaching 4: Filter residue 3 was heated to 800°C for 1 h in a chamber electric furnace (SX-4-10, Tianjin Tester Instrument Co., Ltd), the slag was then transferred to a beaker after cooling, 100 cm³ of 25% nitric acid (HNO₃, AR, Chengdu Jinshan Chemical Reagent Co., Ltd) solution was added, and the filtration was performed after a water bath for 1 h with stirring at room temperature (25°C). Filtrate 4 was used to determine the REEs* in the crandallite phase, and the filter residue 4 was reserved.

3. Results and discussion

3.1. Ore material composition

3.1.1. Chemical composition

3.1.1.1. Chemical composition analysis

The results of chemical multielement analysis (Table 1) show that the main oxides in the ore sample are P_2O_5 , Al_2O_3 , SrO , CaO , SO_3 , Fe_2O_3 , and SiO_2 . The content of P_2O_5 is 21.7%, which indicates that the ore is a low-grade phosphorus ore. The contents of Al_2O_3 , SrO , and TiO_2 are 26.11%, 4.81%, and 1.32%, respectively, are relatively high. Therefore, in addition to the main element P, the elements Al, Sr, and Ti can be used as useful elements for comprehensive recovery. The results indicate that the ore is mainly composed of aluminophosphate mineral formed of P_2O_5 , Al_2O_3 , CaO , and SrO , iron-sulphide minerals formed of SO_3 and Fe_2O_3 , and clay minerals formed of SiO_2 and Al_2O_3 .

Peng et al. (1979) found that the ratio of MnO/TiO_2 is generally less than 0.5 in the shallow sea environment near continents. The ratio of MnO/TiO_2 in the ore sample is 0.01, which indicates that the phosphorus ore in the study area formed in a shallow sea environment near a continent.

Table 1. Results of chemical multi-element analysis (%)

Oxide	Al_2O_3	CaO	TFe_2O_3	P_2O_5	SiO_2	SO_3	SrO
<i>Assay Value</i>	26.11	7.64	14.81	21.70	0.83	28.40	4.81
Oxide	MgO	BaO	K_2O	TiO_2	ZrO_2	MnO	MnO/TiO_2
<i>Assay Value</i>	0.08	0.31	0.08	1.32	0.13	0.01	0.01

3.1.1.2. Trace element analysis

The test results (Table 2) show that the enrichment coefficients of U, Cr, As, and Sb in the ore sample, which are 20.11, 9.43, 48.07, and 12.00, respectively, are markedly higher than those in the upper crust. The enrichment coefficients of Ba, Hf, Nb, Ta, Th, V, W, and Zr are all greater than 1, and the enrichment is obvious. The enrichment coefficients of Cs, Rb, Co, and Ni are less than 1, and the loss is significant.

In modern marine sediments, the enrichments of As and Sb are important signs of hydrothermal sediments (Marchig et al., 1982). The ore is significantly enriched in AS and Sb, indicating that the ore has the characteristics of hydrothermal genesis. Rona (1978) proposed that U/Th is above 1 in hydrothermal sedimentary rocks, but U/Th is below 1 in non-hydrothermal sedimentary rocks. The U/Th in the ore is $1.43 > 1$, which also suggests the ore is affected on a degree by hydrothermal sedimentation.

Both V/Cr and Ni/CO can be used as indicators of paleoredox. Generally, $V/Cr < 2$, $Ni/CO < 5$ in oxidative sedimentary environment, $V/Cr = 2 \sim 4.25$, $Ni/CO = 5 \sim 7$ in oxygen-poor sedimentary environment, $V/Cr > 4.25$, $Ni/Co > 7$ in weakly oxidative or reducing environment (Jones and Manning, 1994). In the ore samples, $V/Cr = 0.33$, and $Ni/CO = 4.78$, signifying that it was formed in oxidative sedimentary environment.

Wang et al. (1979) proved that the ratio of Sr/Ba can also be used as an effective indicator to distinguish marine and continental strata; when $Sr/Ba > 1$, the sediments are marine sediments, and when $Sr/Ba < 1$, they are generally continental sediments. The value of Sr/Ba in the ore sample is 15.20, which is > 1 , thereby also indicating that the phosphorus ore in the study area is related to marine sediments.

3.1.1.3. Characteristics of rare earth composition

The REE contents and the calculation results of related characteristic parameters are shown in Table 3. The total amount of rare earth elements in the ore sample is 2080×10^{-6} , and the REO content is 0.25%, which reaches industrial grade (0.15%) of ion adsorbed rare earth ore (Editorial, 2010). It shows that the ore is significantly enriched in REEs which can be recovered as the useful elements of the ore (Liu, 1994; Huang, 1997; Chen et al., 2019).

The ore is enriched in LREEs, among which La, Ce, and Nd contents are high, i.e., 359×10^{-6} , 298×10^{-6} , 284×10^{-6} , respectively. The LREE/HREE ratio is 1.08, which indicates that the ore is slightly enriched in LREEs. The $(La/Yb)_N$ value is $6.44 > 1$. The normalized REE chondrite distribution curve (Fig. 3) is inclined to the right, showing LREE enrichment. The $(Gd/Yb)_N$ value is $1.57 > 1$, and the $(La/Sm)_N$ value is $3.95 > 1$, which also indicates that the ore is an LREE-enriched type (Zhao, 1985). In addition, the yttrium content is 734×10^{-6} , which accounts for 35.28% of the total REE content, and the enrichment degree is high. In summary, the svanbergite in this mining area has the basic characteristics of LREE and yttrium enrichment.

Table 2. Content of trace element (10^{-6})

Element	Cs	Hf	Nb	Rb	Ta	Cr	Th	U
Ore sample	0.16	17.90	37.90	1.20	2.80	330.00	39.50	56.30
Upper crust	3.70	5.80	12.00	112.00	1.00	35.00	10.70	2.80
Enrichment coefficient	0.04	3.09	3.16	0.01	2.80	9.43	3.69	20.11
Element	V	W	Zr	Ba	As	Sb	Co	Ni
Ore sample	110.00	7.00	669.00	2690.00	72.10	2.40	7.30	34.90
Upper crust	107.00	2.00	190.00	550.00	1.50	0.20	17.00	44.00
Enrichment coefficient	1.03	3.50	3.52	4.89	48.07	12.00	0.43	0.79

Note:

- 1) The abundance value of the upper crust is based on the data in the literature (Chi and Yan, 2007).
- 2) Enrichment coefficient = ore sample element abundance / upper crust element abundance.

Table 3. REEs content and characteristic parameters (10^{-6})

Element	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Content	72.90	10.70	71.80	16.40	46.80	6.36	37.60	5.39
Element	La	Ce	Pr	Nd	Sm	Eu	Y	δU
Content	359.00	298.00	67.50	284.00	57.20	12.70	734.00	0.60
Parameter	$\Sigma LREE$	$\Sigma HREE$	ΣREE	LREE/HREE*	$(La/Sm)_N^*$	$(Gd/Yb)_N^*$	$(La/Yb)_N^*$	δCe
Result	1078.40	1001.90	2080.35	1.08	3.95	1.57	6.44	0.43

Note:

- 1) The calculation method of rare earth element eigenvalues is based on the reference (Zhao Z., 1985.).
- 2) The quantities with * are dimensionless.

Ce is often used as a marker to indicate the redox conditions of ancient sea water. δCe is $0.43 < 1$ in the ore sample, indicating a negative Ce anomaly, which also reflects that the sedimentary environment of phosphate ore in the study area was a seawater oxidation environment (Mcarthur and Walsh, 1984; Shi et al., 2004; Wang et al., 2014). Ce^{3+} in seawater is easily oxidized to Ce^{4+} , and CeO_2 precipitates in the process of transport, which leads to a negative Ce anomaly in ore-forming rocks (Murray et al., 1990).

Under high temperature condition, Eu mainly exists as Eu^{2+} . The ion radius of Eu^{2+} is large, which is not conducive to the replacement with Ca^{2+} , resulting in the separation of Eu from other REEs and negative Eu anomaly (Bau and Moller, 1992; Sun et al., 2014). δEu is $0.6 < 1$ in the ore, which is a negative Eu anomaly. In the mineralization process, due to the participation of submarine hydrothermal solution, the sedimentary environment temperature rises, and Eu^{3+} is reduced to Eu^{2+} , resulting in a negative Eu anomaly.

Previous studies have found that the genesis of Shifang-type phosphate deposit is complex (Duan et al., 1964; Wang and Li, 1988; Huang and Deng, 2011; He, 2021). Ye et al. (1989) stated that the deposit is sedimentary origin. Similarly, the analyses of the study also indicate that svanbergite in the study area is a marine sedimentary-type phosphorus ore.

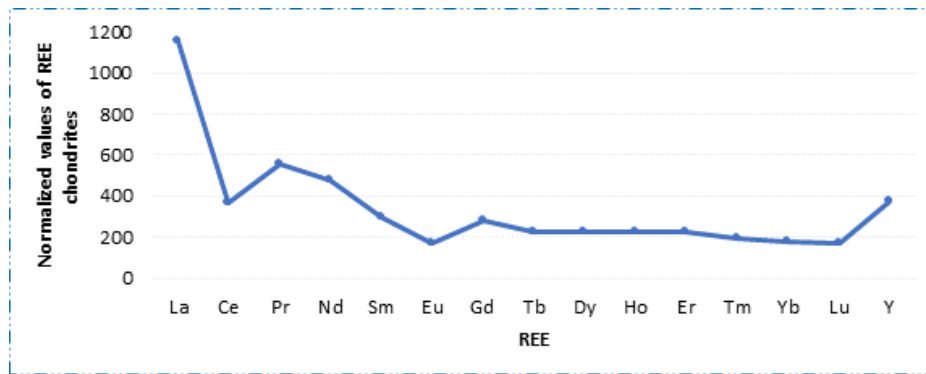


Fig. 3. Normalized distribution pattern of REE chondrites

3.1.2. Mineral composition

The AMICS analysis results (Table 4) show that the ore mineral composition is complex, and the minerals include crandallite, pyrite, apatite, cirrolite, kaolinite, boehmite, and others. Among which crandallite is the main ore mineral, accounting for approximately 86-90% of the total minerals. The energy spectrum of the mineral is shown in Fig. 4. Crandallite can be regarded as the main carrier mineral in terms of the recovery of the useful elements P, Al, Sr, and Ti and is the main valuable mineral in the ore. Apatite, chalcopyrite, and boehmite are secondary useful minerals with a combined total content of 2.06%. Pyrite is the main gangue mineral, accounting for approximately 6-10% of the total minerals. Independent rare earth minerals were not found, which indicates that rare earth elements may exist in the forms of isomorphism or adsorption. It is necessary to determine the occurrence state of rare earth elements by other phase analysis methods.

Table 4. Analysis results of mineral composition by AMICS

Mineral	Molecular formula	Weight percent (%)
Boehmite	AlO(OH)	0.07
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	0.09
Apatite	Ca ₅ (PO ₄) ₃ F	0.44
Cirrolite	Ca ₃ Al ₂ (PO ₄) ₃ (OH) ₈	1.15
Crandallite containing Sr	CaAl ₃ Sr _{0.15} (OH) ₆ P ₂ O ₇ (OH)	11.77
Crandallite containing Sr and Ti	CaAl ₃ Sr _{0.2} Ti _{0.05} (OH) ₆ P ₂ O ₇ (OH)	74.33
Unknown minerals	—	1.41
Pyrite	FeS ₂	5.96
Pyrite Mix Crandallite	Ca _{2.54} Fe _{12.39} Al _{10.87} Sr _{19.74} P _{5.07} O _{41.50}	4.78

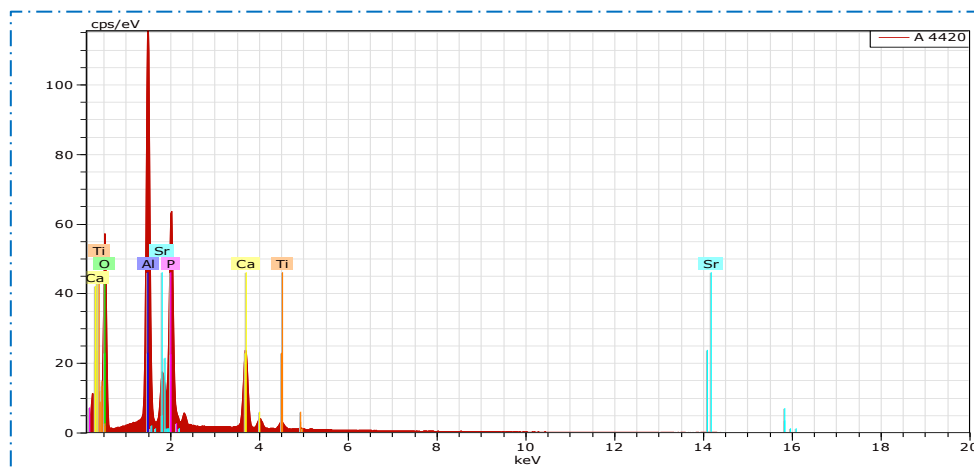


Fig. 4. The energy spectrum of crandallite

However, Some studies have found that the main ore mineral is svanbergite (Duan et al., 1964; Liu and Liu, 1989; Ding et al., 2016) or goyazite (Ye et al., 1989), these two minerals and crandallite all belong to crandallite-type minerals (Wang et al., 1982). Due to the ores for researches come from different mining areas, it is inferred that the differences of sedimentary environment in the process of mineralization leads to the different types and degrees of cation (Rloand et al., 2000), resulting in the difference of main mineral in the ore.

3.2. Ore elements distribution

3.2.1. Distribution of main elements

The distribution of major elements in the ore obtained by AMICS analysis is shown in Fig. 5. Approximately 98% of P is in the form of crandallite, and a small amount of P is distributed in the form of cirrolite and apatite. Approximately 99% of Al exists in crandallite, and a small amount of Al is distributed in kaolinite, chalcopyrite, and boehmite. S and Fe mainly constitute pyrite. Sr and Ti are all present in crandallite. All F exists in apatite, forming fluorapatite. Therefore, crandallite is the main mineral carrier of the useful elements P, Al, Sr, and Ti, and it is the main object of separation and recovery when recovering useful elements.

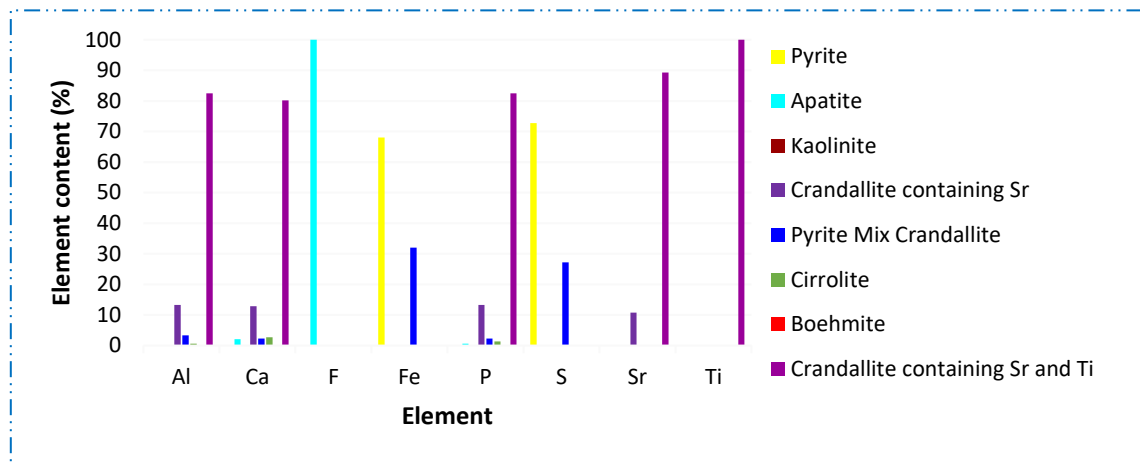


Fig. 5. Distribution of major elements in the ore by AMICS

3.2.2. Chemical phase analysis and phase distribution of REEs

The chemical phase analysis results and phase distribution of REEs are shown in Table 5 and Fig. 6, respectively. Approximately 79% of REEs* (1051.56×10^{-6}) are distributed in the crandallite phase, only a small amount of REEs* ($286.88.56 \times 10^{-6}$) are contained in the adsorption phase and other mineral phases, and independent rare earth minerals were not found in the mineral composition analysis. There are three main occurrence states of elements in ore, such as independent minerals, isomorphism, and adsorption forms (Liu and Fan, 2006). Consequently, it can be judged that rare earth elements mainly occur with the form of isomorphism in crandallite.

Furthermore, crandallite compounds have a strong cation replacement ability: REEs can replace Ca^{2+} and H^+ , Sr^{2+} can replace Ca^{2+} , Ti^{4+} can replace Al^{3+} and H^+ , and HTiO_4^{3-} can replace PO_3^{3-} (Rloand et al., 2000). This further shows that REEs, Sr, and Ti mainly exist in isomorphous forms in crandallite. In this case, it is difficult to separate REEs from the ore by mechanical beneficiation, hydrometallurgical separation is more feasible (Chi and Wang, 2014).

3.3. Distribution characteristics of the main minerals

3.3.1. Particle size distribution characteristics

As shown in Fig. 7, the particle size distributions of the main minerals in the ore are as follows: 60% of the crandallite particles range in size from 100 μm to 200 μm and are mainly characterized by fine-grained distributions. For boehmite, 80% of the particles are less than 120 μm , and it is mainly fine-

grained. The particle size of 60% of cirrolite particles is 12-300 μm , and this mineral is mainly fine-grained and unevenly distributed. The particle sizes of 80% of pyrite, kaolinite, and apatite are all less than 30 μm , and 80% of particles of pyrite mixed with crandallite are less than 11 μm ; they are all mainly distributed as microparticles. The analysis results show that the disseminated grain size of the main minerals in the ore is relatively fine (XU, S., 1981). In particular, the particle size of pyrite is extremely fine, flotation recovery of pyrite not only increases grinding energy consumption, but also makes the process flow more complicates.

Table 5. Chemical phase analysis results (10^{-6}) and phase distribution rate (%) of REEs

REEs phase	Y	La	Ce	REE*	Distribution
Ion adsorption phase	42.80	11.11	0.00	53.91	4.23
Apatite phase	54.76	8.89	0.00	63.64	4.99
Pyrite phase	80.84	21.33	3.73	105.91	8.31
Crandallite phase	478.31	316.89	256.36	1051.56	82.47
Total	700.13	378.22	260.09	1275.02	100.00
Raw ore grade ($\mu\text{g/g}$)	734.00	359.00	298.00	1391.00	
Error (%)	-4.61	5.35	-12.72	-8.34	

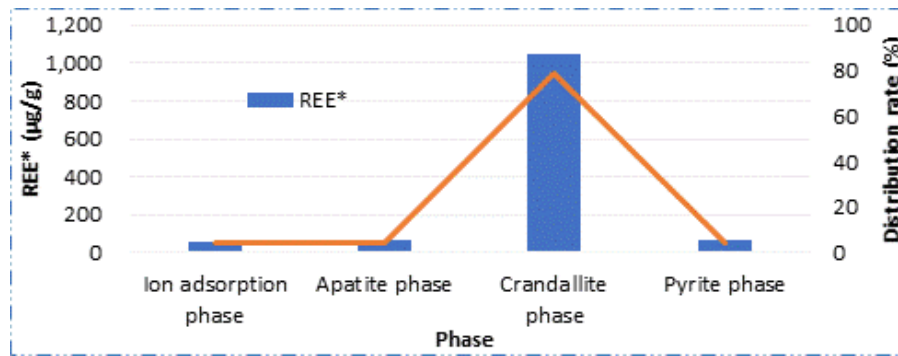


Fig. 6. Chemical phase analysis results of REEs

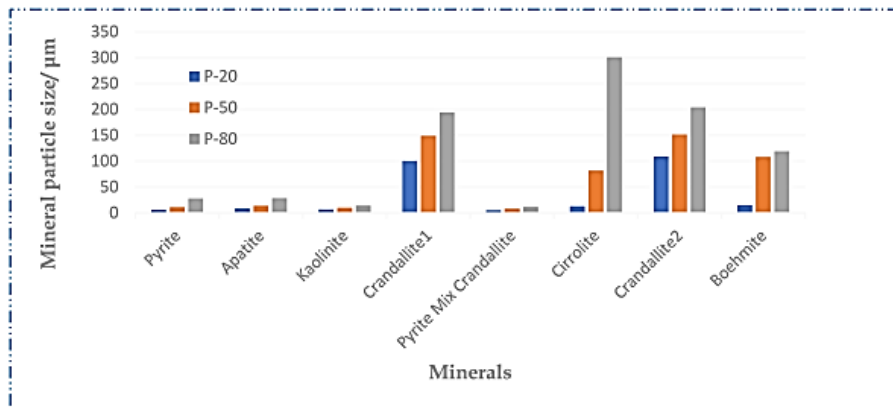


Fig. 7 Particle size distribution of main minerals in the ore by AMICS (P-50 indicates that 50% of the particles are smaller than the corresponding mineral particle size in the histogram; crandallite 1: crandallite containing Sr; crandallite 2: crandallite containing Sr and Ti)

3.3.2. Embedded features

The classified view seen in Fig. 8 (a) and BSE view seen in Fig. 8 (b) of the ore minerals by AMICS show that crandallite is finely cryptocrystalline, and a small fraction of the crandallite is closely associated with pyrite particles. This fraction is not easy to recover by the physical separation method and needs

to be treated with metallurgical or chemical methods. Pyrite is dissolved and metasomatized to metasomatic residual or heteromorphic granular by apatite, kaolinite, and aluminite, and it is unevenly dispersed in the crandallite. Cirrolite features an uneven stellate distribution in the crandallite. it can be concluded that the mineral dissemination of the ore is very close. In other words, the composition of the ore is complex, the minerals are closely related, and the disseminated grain size is fine. It is necessary to consider the occurrence state of P, rare earth elements, Al, Sr, and Ti in the ore and then formulate a reasonable test scheme for the comprehensive recovery of useful elements.

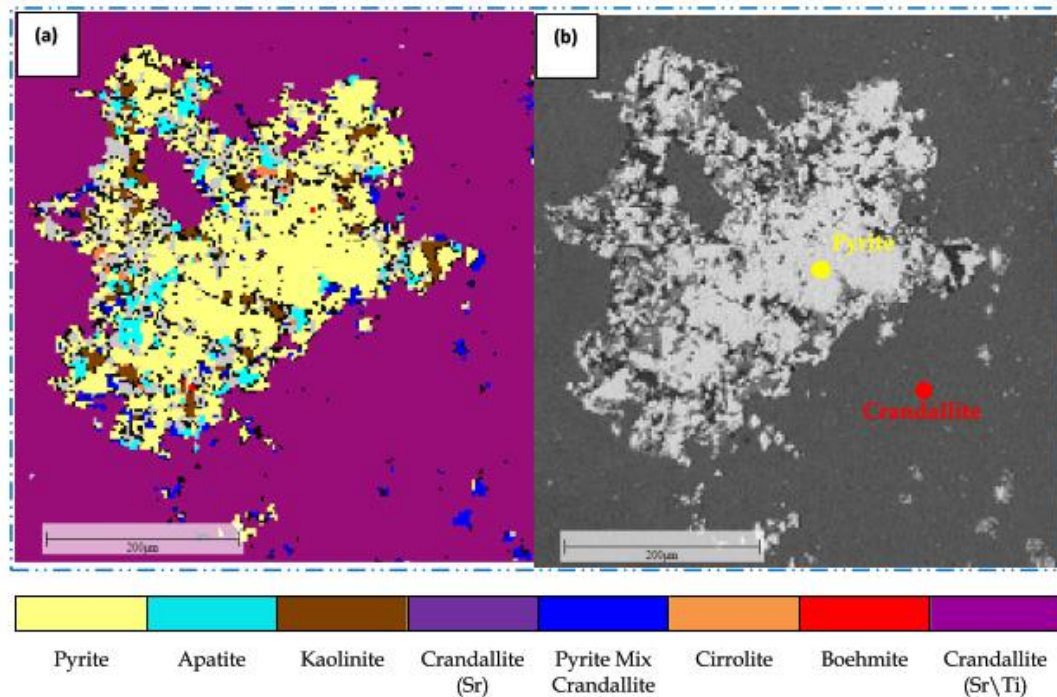


Fig. 8. Classified view (a) and BSE view (b) of the ore minerals by AMICS

The classified view seen in Fig. 8 (a) and BSE view seen in Fig. 8 (b) of the ore minerals by AMICS show that crandallite is finely cryptocrystalline, and a small fraction of the crandallite is closely associated with pyrite particles. This fraction is not easy to recover by the physical separation method and needs to be treated with metallurgical or chemical methods. Pyrite is dissolved and metasomatized to metasomatic residual or heteromorphic granular by apatite, kaolinite, and aluminite, and it is unevenly dispersed in the crandallite. Cirrolite features an uneven stellate distribution in the crandallite. it can be concluded that the mineral dissemination of the ore is very close. In other words, the composition of the ore is complex, the minerals are closely related, and the disseminated grain size is fine. It is necessary to consider the occurrence state of P, rare earth elements, Al, Sr, and Ti in the ore and then formulate a reasonable test scheme for the comprehensive recovery of useful elements.

3.4. Preliminary experiments

According to the above analysis, crandallite is the main treatment object in comprehensive ore utilization to recover the main elements P and rare earth elements and comprehensively recycle Al, Sr and Ti. However, the extraction methods of rare earth elements and related elements need to be further studied.

In view of the fine disseminated particle size of the ore minerals, fine grinding is needed to improve the liberation degree of the useful minerals to improve separation recovery. However, the finely disseminated minerals are closely related, and excessive fine grinding not only affects the physical separation effect but also increases the production cost. Xu (1981) also suggested that the fine-grained minerals need chemical treatment when the ore properties are complex. Moreover, the content of crandallite in the ore is high, so it is unnecessary to increase the separation and enrichment process of the concentration of crandallite. In addition, crandallite is easily dissolved by acid after roasting (Wang,

1991; Yu et al., 2008). In this context, we have conducted preliminary experiments on leaching of rare earth with acid from svanbergite and its roasting product, respectively.

The leaching test shows that under the leaching conditions of an acid concentration of 25%, a liquid-solid ratio of 100 cm³/g, a particle size-75 μm, a reaction temperature of 25°C, and a reaction time of 60 min, the leaching rate of rare earth elements was only approximately 36% when the ore is leached with nitric acid. However, when the ore was roasted at 800°C for 60 min, and then leached with nitric acid and phosphoric acid (H₃PO₄, AR, Tianjin Oubokai Chemical Co., Ltd), the leaching rate of rare earth elements both reached more than 80%. With the above analysis and preliminary experiments, the method of roasting and acid leaching to recover REEs from svanbergite is feasible and effective (Lokshin, et al., 2013; Lokshin, et al., 2015; Orabi et al., 2018; Lou et al., 2018a; 2018b; Ye et al., 2020).

4. Conclusions and recommendations

(1) The svanbergite in the study area represents marine sedimentary low-grade phosphorus ore, which is rich in rare earth elements, aluminum, and strontium. Crandallite, with a content of 86-90%, is the main useful mineral in the ore and is the main carrier mineral of P, REEs, Al, Sr, and Ti, and it is the main treatment object for comprehensive recovery of useful elements.

(2) Independent rare earth minerals were not found in the ore, whereas a small amount of ion-adsorbed rare earth elements were found. REEs mainly occurs via isomorphism in crandallite.

(3) The disseminated ore minerals are closely associated, and the disseminated grain size of the minerals are relatively fine. It is feasible to recover REEs by roasting and acid leaching.

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