

Article

Genesis of Pyrite in Clastic Rocks of Deep Salt-Related Strata in the Simao Basin and Its Implication for Potash Mineralization: A Case Study of the Well MK-3

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Abstract: In depth of the Simao Basin (2390 to 2650 m depth interval), many gray mudstone or carbonate rocks are developed in the red salt-related strata, and pyrite crystals are found in the fissure and matrix. In this study, petrology, mineralogy, element geochemistry, and LA-MC-ICP-MS in situ sulfur isotope analysis were used to constrain the genesis of pyrite, and the influence of relevant geological activities on potash mineralization was discussed. The results show that: (1) In the upper part of the salt layer, particle size of the pyrite ranges from 50 to 300 μm . The crystal morphology is mainly pentagonal-dodecahedral and irregularly granular, with a small amount of cuboidal pyrite. In the interlayer between rock salt, particle size of the pyrite is from 50 to 100 μm , and the crystals are mainly octahedral. (2) The S/Fe value of pentagonal-dodecahedral pyrite is significantly greater than 2; the S/Fe value of octahedral and cubic pyrite is less than 2; and the S/Fe value of irregular granular pyrite is close to 2. (3) The $\delta^{34}\text{S}_{\text{V-CDT}}$ values of pyrite in the upper salt-related strata range from -15.65‰ to 11.81‰ , and the average $\delta^{34}\text{S}_{\text{V-CDT}}$ values of all samples range from 0.79‰ to 8.20‰ . The $\delta^{34}\text{S}_{\text{V-CDT}}$ values of pyrite interlayer between rock salt range from -15.02‰ to -6.36‰ , with an average value of -10.66‰ . The above results indicate that the pyrite in the upper part of the rock salt layer was formed in a medium-low temperature hydrothermal environment, and the ore-forming sulfur elements have hydrothermal sources, bacterial sulfate reduction (BSR) sources, and thermochemical sulfate reduction (TSR) contributions. The pyrite between the rock salt layers is of sedimentary origin, and the ore-forming sulfur element comes from BSR. At present, there is no evidence of the influence of hydrothermal activities on deep potash-rich salt bodies, and the influence on the Mengyejing potash deposit has continued since the metallogenic period.

Keywords: Simao Basin; potash; pyrite; sulfur isotope; in situ analysis; hydrothermal activity



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1. Introduction

The Mengyejing potash deposit (MPD) in the Simao Basin is the only ancient chloride-type potash deposit in China. The proven distribution area of rock salt in the mining area is 3.5 km², among which the distribution area of potash is 2.8 km², the average KCl content of the potash ore beds is 8.81%, and the KCl reserves are $1676.04 \times 10^4 \text{ t}$ [1].

Recently, important progress has been made in the investigation of deep potash outside the mining area. Potash-rich rock salt with a cumulative thickness of 149 m was discovered at a depth of 2390 to 2650 m, and the maximum content of KCl can reach 13.4% [2,3]. Miao et al. [3] proved that the provenance of the rock salt was seawater by analyzing the strontium (Sr), sulfur (S), and potassium (K) isotopic geochemical characteristics of the rock salt and its related anhydrite rocks. Du et al. [4] also reached the same conclusion by analyzing the geochemical characteristics of trace elements and chlorine (Cl) isotopes in rock salt. Song et al. [5] analyzed the geochemical characteristics of trace elements in the brownish-red clastic rocks in the salt-related strata and concluded that the “red bed” in salt

was deposited in a weak oxidizing environment, with a hot and arid paleoclimate, strong evaporation of lake basin water, and high salinity.

In salt-related strata, grayish green, gray, dark gray, and grayish black mudstone and carbonate rocks are also developed, with argillaceous structure, horizontal bedding, bedding detachment structure along the striated layer, and cracks formed along the detachment plane. The pyrites are present in the filling of the bedding fault and in the mudstone matrix.

Based on the analysis of petrological characteristics of core samples in the gray bed of deep salt-related strata in the well MK-3 (located in southeastern Simao Basin, see map in Figures 1 and 2), this study combined with the crystal morphology of pyrite, relative element contents of S and ferrum (Fe), and in situ sulfur isotope analysis, discussing the genetic mechanism, sedimentological significance of pyrite, and its influence on salt deposits already formed in the study area. Among them, the LA-MC-ICP-MS method is used for in situ sulfur isotope analysis of pyrite, which can not only obtain accurate sulfur isotope values but also reveal the similarities and differences of sulfur isotopes between different crystals, to trace the source of sulfur elements and related geological processes more precisely. The study of the genesis of pyrite is helpful to understand the material sources of sulfur, hydrothermal properties, and activity periods [6–9], which can provide the basis for exploring the enrichment and mineralization mechanism of potash.

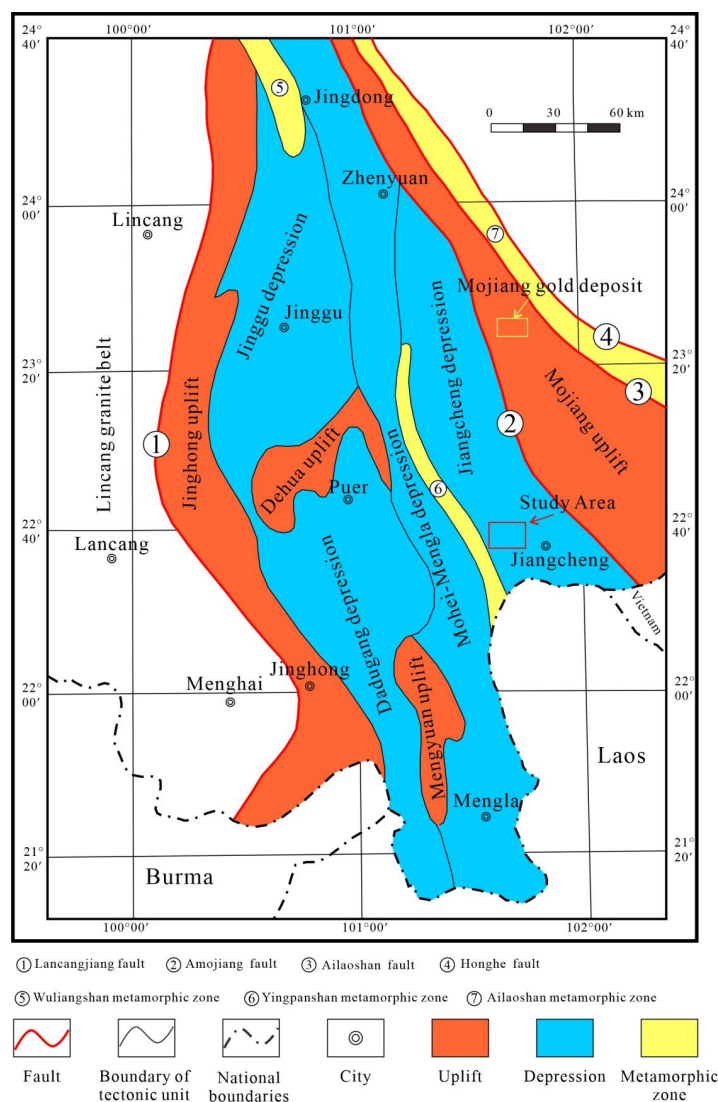


Figure 1. Geographical location of Simao Basin and research area, division of tectonic units, and distribution of main faults in basin.

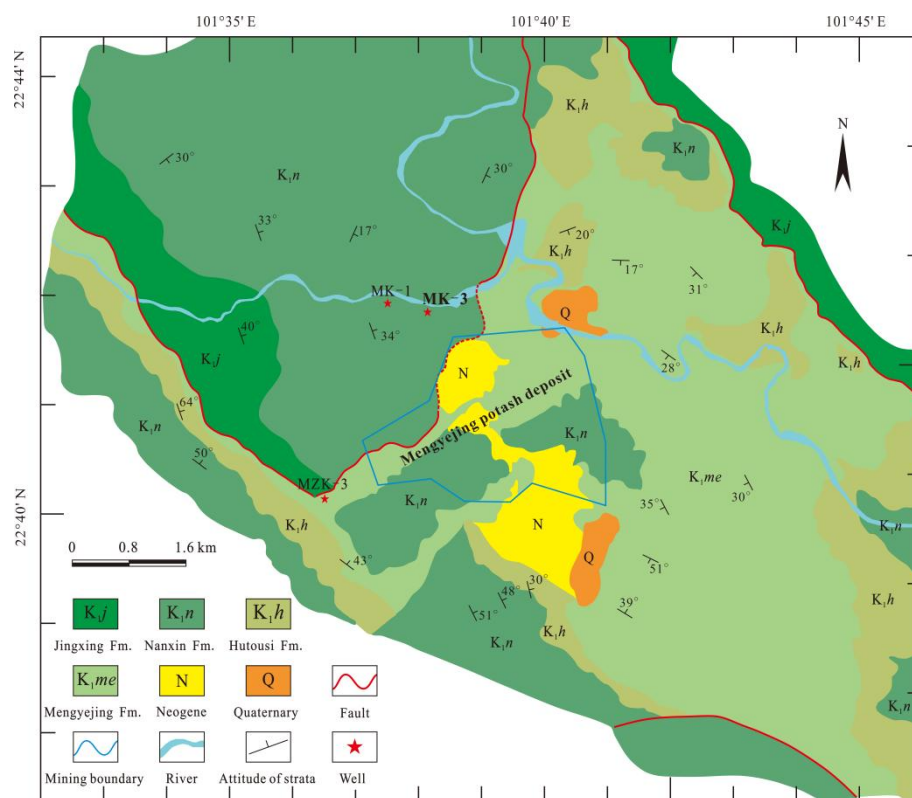


Figure 2. Geographical location and geological map of the Mengyejing Potash deposit in the Simao basin, containing the location of the wells MK-1 and MK-3.

2. Geological Setting

The Simao Basin is located in the northern part of the Indo-China block [10] and tectonically belongs to the Sanjiang Orogenic belt [11]. The eastern and western boundaries of the basin are the Jinshajiang-Ailaoshan fracture zone and the Lancangjiang fracture zone [12].

The Simao Basin can be divided into four uplifts and four depressions, a total of eight second-order tectonic units (see Figure 1), and the sedimentary strata are mainly Mesozoic-Cenozoic [13,14]. Salt rocks discovered in the basin are mainly found in the Mengyejing Formation of the Lower Cretaceous, with a maximum burial depth above 1251 m. From west to east, salt rocks can be divided into the Jinggu salt-bearing belt, Zhengdong-Mengla salt-bearing belt, and Jiangcheng salt-bearing belt [2,15]. The surrounding rock of salt rock is mainly mud-clast conglomerates, and there is no carbonate rock and sulfate rock of corresponding scale in normal evaporative deposition sequence, and mud-clast conglomerates often appear in salt rock [16,17]. The potash deposit occurs in the Mengyejing area of the Jiangcheng salt-bearing belt in the southeast of the basin, and the ore beds are produced in the upper member of the Mengyejing Formation [18–20].

MPD is developed in a syncline, and the outcrop strata around the mining area are as follows: Lower Cretaceous Jingxing Formation, Nanxin Formation, Hutousi Formation, Mengyejing Formation, Neogene, and Quaternary. The dip angle is 17° to 64°, and the main lithology is fluvatile-lacustrine sandstone (see Figure 2). Two exploration wells numbered MK-1 and MK-3 were deployed in the area of 500 to 1000 m northwest of the mine to explore the occurrence of deep potash. Potash-rich rock salt was found below 2000 m in both wells. Among them, the well MK-1, which was completed in 2012, drilled a 70 meter-thick potassic-bearing salt rock at a depth of 2253 to 2323 m. The well MK-3, completed in 2019, found two potash-bearing rocks with a cumulative thickness of 149 m at depths of 2397 to 2443 m and 2542 to 2645 m.

The tectonic evolution of Tethys has a strong influence on the lithology and lithofacies of sedimentary cover in the Simao Basin. From Devonian to Late Triassic, the Paleo-Tethys developed from formation to shrinkage, and the sedimentary cover in the basin was mainly marine clastic rocks and limestone [21,22]. Since the Jurassic, the basin has been characterized by continental red beds, mainly composed of fluvial or lacustrine sandstone, shale, conglomerate, and coal seam [14]. The occurrence of marine limestone and bivalve fossils in the Middle Jurassic in the western margin of the basin reflects a transgression of the Middle Tethys [23]. The deposit of marine halite and potash was found in the continental Mengyejing Formation of the Lower Cretaceous, which indicates that diapir occurred in the ancient salt rock with seawater as a source during the Tethys closure process [1].

Since the Cenozoic era, under the influence of the collision between the Indian plate and the Eurasian plate, the Indo-China block has undergone a clockwise rotation relative to the modern magnetic field, rotating clockwise from near east–west to the present northwest–southeast direction [24,25]. Strike-slip and thrust nappe structures occurred within the continental block, and the fault system developed [26], and the formed salt deposits were technologically deformed or hydrothermal reformed [1,27].

3. Samples and Methods

3.1. Samples

Samples were collected from the well MK-3 with wellhead coordinates 101°37′43.5″ E and 22°41′25.0″ N (see Figure 2). The started stratum of the well MK-3 is the Lower Cretaceous Nanxin Formation, and the Lower Cretaceous Jingxing Formation was drilled at a depth of 536.5 m, and its characteristic is gray and white sandstone with coal line. The Upper Jurassic Bazhulu Formation, which is characterized by brown-red mudstone, was drilled at a depth of 1586.0 m. The Middle Jurassic Hepingxiang Formation, characterized by brownish-red fine clastic rocks with grain-green calcitic mudstone, mudstone, and anhydrite clots, was drilled at a depth of 1658.2 m, and the well completion of Hepingxiang Formation was at a depth of 2701.0 m (see Figure 3). Thirteen samples were taken from well MK-3 at depths of 2358.0 to 2530.0 m, including 12 samples above the salt layer and 1 sample between the salt layer (see Figure 4). The main color of the sample is gray or gray-green, and the main lithology is mudstone and carbonate rock (see Figure 5).

3.2. Methods

3.2.1. Thin Section Identification of Whole Rock Samples

The whole rock sample was fixed on the slide with epoxy resin as the binder, and the sample was ground into 0.03 mm thick. The sample was observed under a polarizing microscope. The polarizing microscope model is Leica 2700P (Leica Microsystems Wetzlar GmbH, Wetzlar, Germany), with an LED (light-emitting diode) light source, and the image acquisition system is a LAS (Leica Application Suite) imaging module.

3.2.2. Mineral Composition Analysis of Whole Rock Samples

Whole rock samples were crushed to 200 mesh without fracture filling and then prepared for analysis. The instrument model is a Panalytical X'Pert PRO X-ray diffractometer (Panalytical Company, Almelo, The Netherlands); the radiation is Cu target; the tube voltage/current is 40 kV/40 mA; the step length is 0.02°; and the scanning angle is 5°~70°.

About quantitative analysis of the mineral content of the whole rock, the relative deviation is less than 10% when mineral content is greater than 40%; the relative deviation is less than 20% when mineral content ranges from 20 to 40%; the relative deviation is less than 30% when mineral content ranges from 5 to 20%; the relative deviation is less than 40% when mineral content less than or equal to 5%.

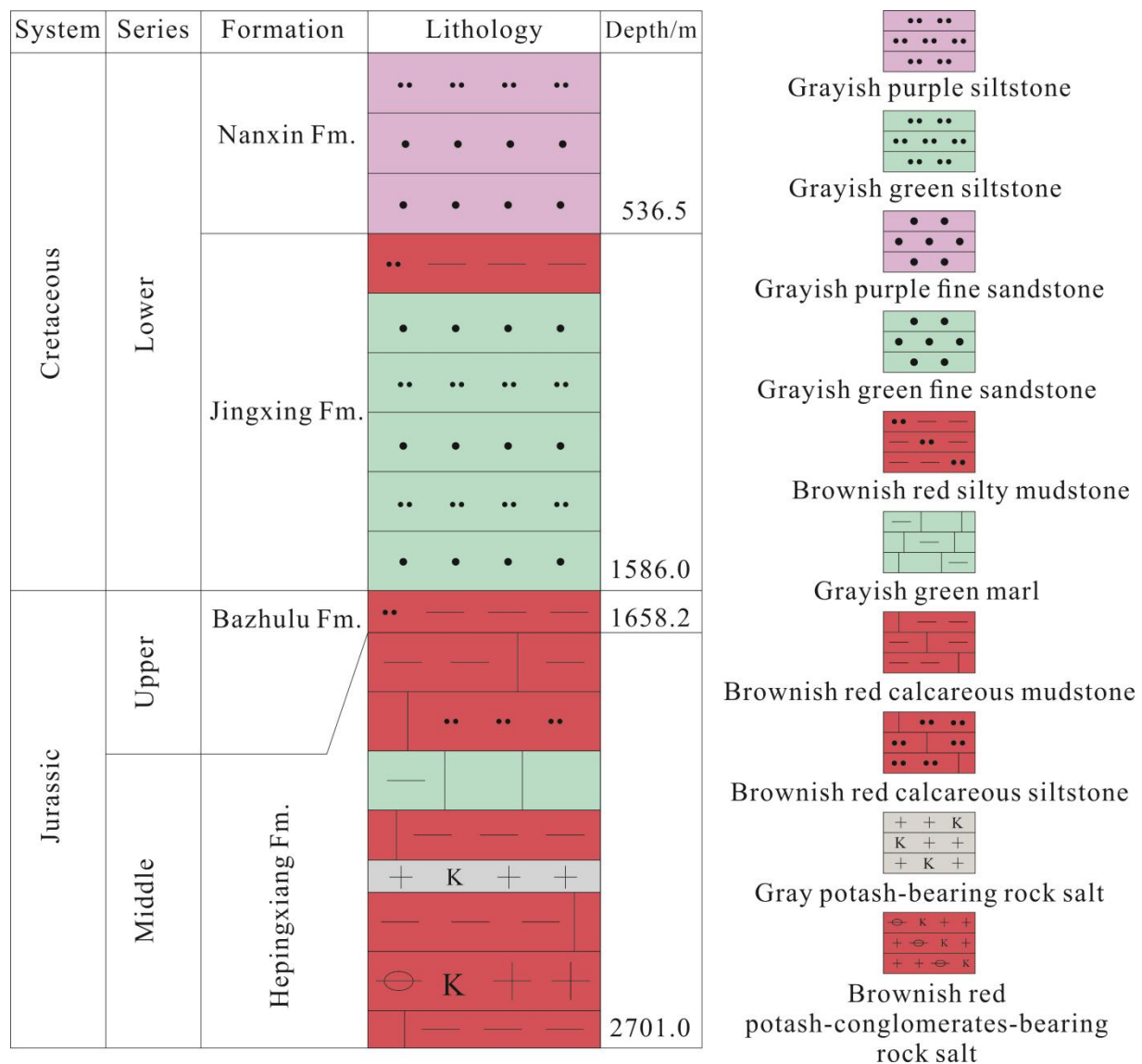


Figure 3. Stratigraphic sequence, lithology, and depth boundary drilled by the well MK-3 in the Simao Basin.

3.2.3. Scanning Electron Microscope and Energy Dispersive Spectrometer

The scanning electron microscope (SEM) model used in this study is a Hitachi TM3030 (Hitachi Limited, Tokyo, Japan) with a digital image processing system, and the energy dispersive spectrometer (EDS) is a Quantax 70 (Bruker Corporation, Billerica, MA, USA). The quantitative analysis method is standardless quantitative analysis with normalization to 100%. The specific method is as follows: first, the conductive tape is bonded to the sample column, and then the sorted pyrite particles are glued to the tape. Then, the sample column is placed on the sample support to adjust the height, so that the distance between the height of the sample surface and the scale is about 1 mm. Finally, the sample support is put into the sample chamber for testing.

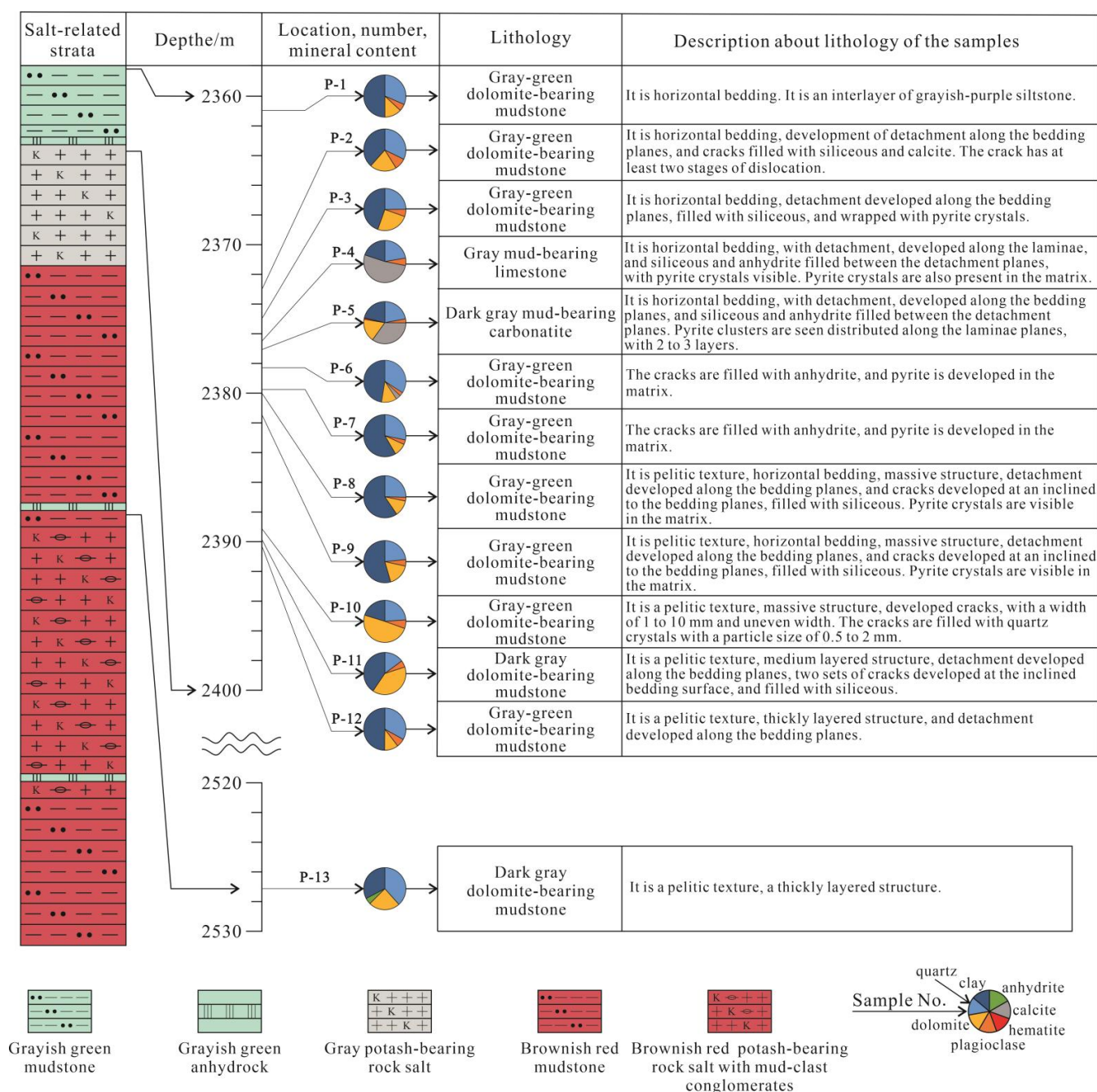


Figure 4. Sampling location and description of the lithology of salt-related strata in well MK-3, Simao Basin.

3.2.4. In Situ Analysis of Sulfur Isotopes

The sulfur isotope composition of pyrite in situ was measured by laser denudation multi-receiving cup inductively coupled plasma mass spectrometry (LA-MC-ICP-MS), from the Institute of Mineral Resources, Chinese Academy of Geological Sciences (CAGS), Beijing, China. The laser denudation system is Resolution S155, and Neptune Plus is the MC-ICP-MS. Laser denudation systems use helium as carrier gas. A single point mode was used in the analysis, and a large beam spot (40 to 50 microns) and low-frequency (4 Hz) laser conditions were selected to ensure a stable signal under low-frequency conditions. The laser energy density is fixed at 5.0 J/cm². The Mass Spectrometer Neptune Plus is equipped with 9 Faraday cups and 10¹¹ Ohmic resistance amplifiers. The medium resolution mode (≈ 7000) is adopted to remove the influence of interference peaks. Three Faraday cups (C, H1, and H2) are used to receive ³²S statically. For ³³S and ³⁴S signals, isotopic fractionation

was corrected by the SSB method. Using pyrite reference Balmat [28] and YP136 [29], the accuracy of $\delta^{34}\text{S}$ analysis is better than 0.5‰.

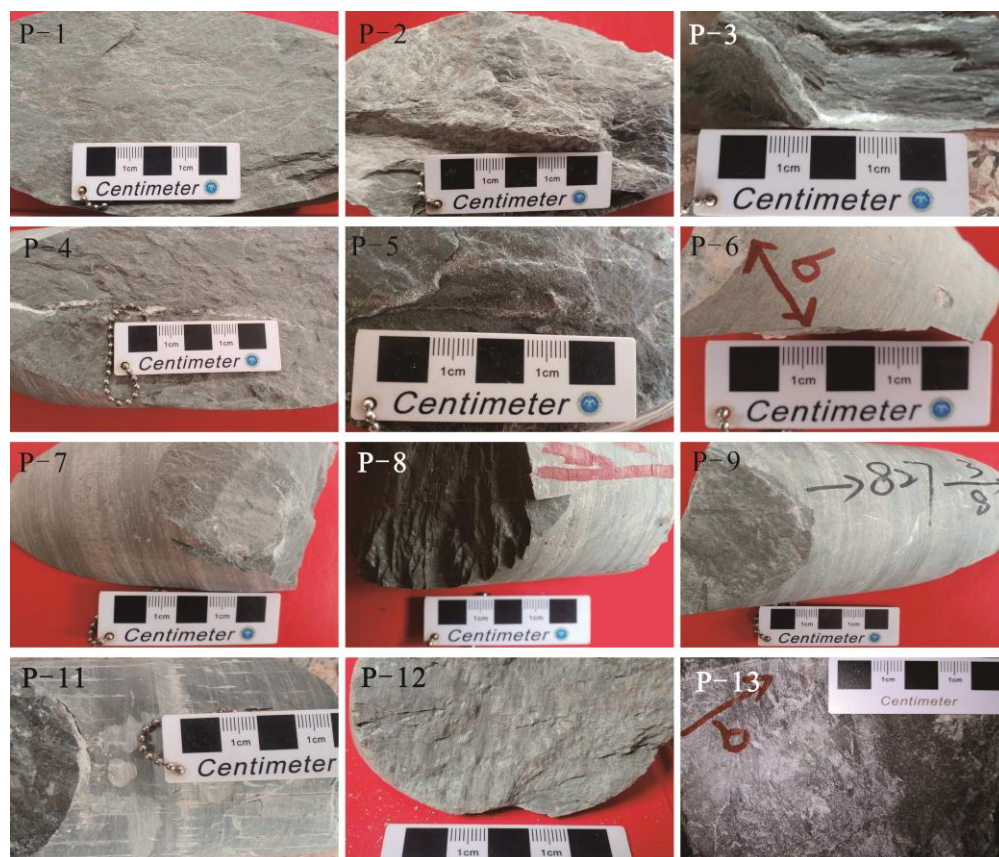


Figure 5. Sample photos of the salt-related strata of the well MK-3, Simao Basin.

The sulfur isotope values of three pyrite crystals were measured in sample P-1. The sulfur isotope values of 15 to 30 pyrite crystals were measured in the rest of the samples.

4. Results

4.1. Petrological Characteristics of the Sample

The diameter of the core sample is 70 mm. The appearance of the core sample is gray, dark gray, and gray-green, which is distinctive in the red of the main part of the clastic rock in salt-related strata. The clastic rock samples showed an argillaceous structure (see Figure 6a), and the carbonate rock samples showed a cryptocrystalline structure. Horizontal bedding (see Figure 6b) can be observed in the samples, and detachment structures are developed along the bedding plane (see Figure 5, P2-5, P-8, P-11, and P-12). The fractures formed by detachment are filled with siliceous, dolomite, or calcite. Two groups of fractures are developed in the way of an oblique crossing the bedding plane, filled with siliceous (P-3, P-4, and P8-11) or siliceous and calcite (P-2) or siliceous and dolomite (P-5) or dolomite (P-6).

Pyrite exists in three forms in core samples: (1) in the form of inclusion in the siliceous fillings along the stratified detachment fissure (P-3 and P-4), (2) scattered in a mudstone matrix (P-4, P-6, P-8, and P-9), and (3) distributed along the surface of the lamina (P-5).

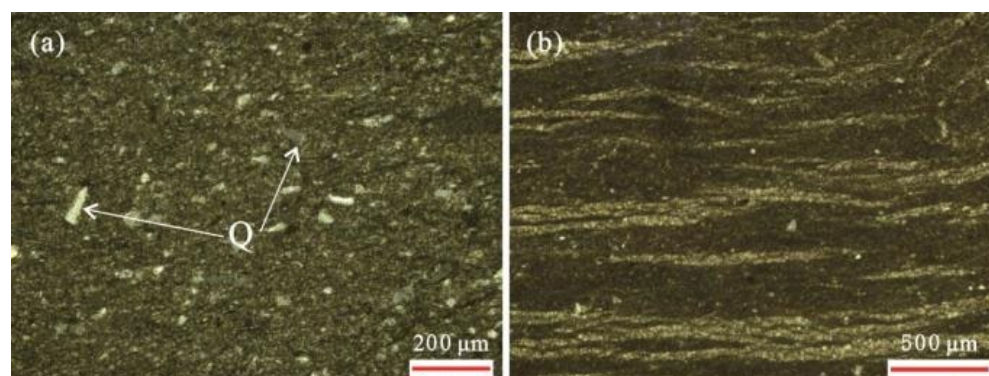


Figure 6. Microscopic photos of samples from the well MK-3 in Simao Basin. (a) Sample No. MK-3-P-6 (Gray-green dolomite-bearing mudstone), fine quartz particles; (b) Sample No. MK-3-P-11 (Dark gray dolomite-bearing mudstone), horizontal lamination. Q-quartz.

4.2. Whole Rock Mineral Composition

The results obtained by X-ray diffraction analysis of the whole rock mineral composition of the sample are shown in Table 1. As can be seen from Table 1, the main mineral components of the sample are quartz, plagioclase, clay minerals, dolomite, calcite, and hematite (P-3) or anhydrite (P-13), which can be detected in individual samples. Sample No. P-4 contains 52% calcite and is designated as argillaceous limestone. The sum of calcite and dolomite content of sample No. P-5 is 52.5%, so it is designated as argillaceous carbonate rock. Sample No. P-10 contains 49.3% dolomite, slightly lower than the content of clastic minerals, and is designated as dolomitic mudstone. The remaining samples have an absolute preponderance of detrital minerals and are named dolomite-bearing or dolomitic mudstone according to the relative content of dolomite.

Table 1. Whole rock mineral composition of pyrite-bearing strata in Well MK-3.

S.N.	No.	Depth/m	Lithology	Relative Mineral Content/wt%						
				Qtz.	Pl.	Cal.	Dol.	Hem.	Anh.	C.M.
1	P-1	2360.8	D.B.M.	31.5	5.4	/	13.0	/	/	50.1
2	P-2	2373.2	D.B.M.	32.2	8.9	/	20.5	/	/	38.4
3	P-3	2374.9	D.M.	24.8	5.6	/	25.0	/	/	44.6
4	P-4	2376.4	A.L.	22.4	5.7	52.0	/	/	/	19.9
5	P-5	2377.2	A.C.R.	22.1	3.0	34.8	17.7	1.1	/	21.3
6	P-6	2378.2	D.B.M.	34.1	2.9	3.8	11.7	/	/	47.5
7	P-7	2379.7	D.B.M.	28.3	3.5	/	9.7	/	/	58.5
8	P-8	2380.0	D.B.M.	25.4	2.9	/	12.2	/	/	59.5
9	P-9	2381.4	D.B.M.	23.4	5.0	/	17.1	/	/	54.5
10	P-10	2388.9	D.M.	23.9	6.6	/	49.3	/	/	20.2
11	P-11	2389.7	D.M.	14.8	5.2	/	39.5	/	/	40.5
12	P-12	2390.2	D.B.M.	33.1	6.5	/	10.6	/	/	49.8
13	P-13	2527.3	D.B.M.	38.4	/	/	24.1	/	4.8	32.7

S.N.—Sequence Number; No.—number; D.B.M.—dolomite-bearing mudstone; D.M.—dolomitic mudstone; A.L.—argillaceous limestone; A.C.R.—argillaceous carbonate rock; Qtz.—quartz; Pl.—plagioclase; Cal.—calcite; Dol.—dolomite; Hem.—hematite; Anh.—anhydrite; C.M.—Clay mineral.

4.3. Crystal, Elemental, and Sulfur Isotope Characteristics of Pyrite

Microscopically, pyrite exists in micro-cracks as pentagonal-dodecahedron and in the matrix as irregular grains (see Figure 7). Under SEM, not only typical pentagonal-dodecahedral pyrite crystals (see Figure 8a) but also irregular pyrite crystals (see Figure 8b), typical octahedral pyrite crystals (see Figure 8c), and cubic pyrite crystals were observed. In addition, corrosion pits can be observed on the surface of some pyrite crystals. (see Figure 8d).

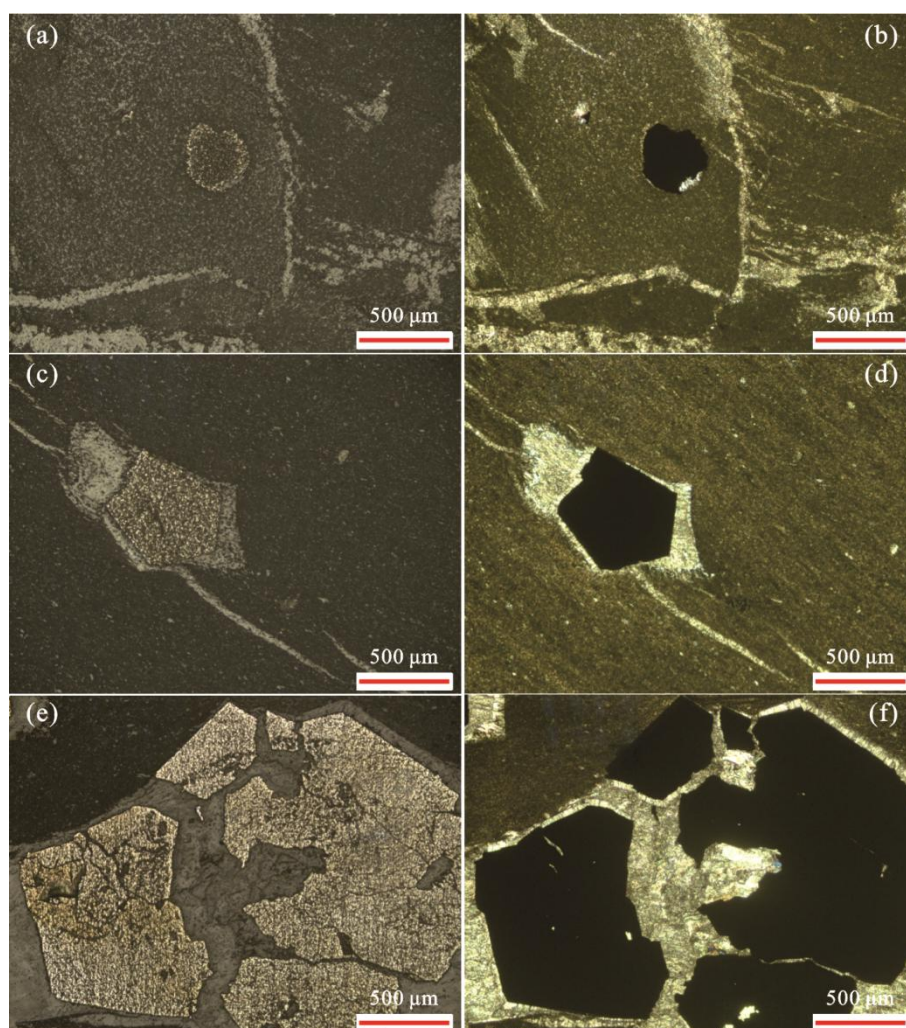


Figure 7. Crystal characteristics of pyrite in the well MK-3, Simao Basin (a) Sample No. P-12, Reflected light of irregular granular pyrite in mudstone matrix; (b) Is a photograph of transmitted light in the same field of view as (a); (c) Sample No. P-12, Reflected light photographs of pentagonal-dodecahedron pyrite in microfracture; (d) Is a photograph of transmitted light in the same field of view as (c); (e) Sample No. P-3, Reflected light photos of pentagonal-dodecahedron pyrite crushed in microfracture; (f) Is a transmitted light photograph in the same field of view as (e) Dolomite precipitated in the later stage cemented the broken pyrite.

Pentagonal-dodecahedron and cuboidal pyrite are mainly distributed in the middle of the sampling depth interval that locates above the rock salt layer in the well MK-3, and the pyrite at the top and bottom of the interval is mainly irregular granular. Octahedral pyrite was present in sample No. P-13, located between two layers of salt rock drilled in well MK-3. Some irregular granular pyrite preserved traces of original cube crystals (see Figure 8d).

Pyrite crystal size ranges from 50 to 300 μm (Table 2). The S/Fe ratios of pyrite with different crystal types are significantly different. For example, the S/Fe ratios of pyrite with a pentagonal-dodecahedral shape are more than 2.0, with an average ratio of 2.18. The S/Fe ratios of the cubic and octahedral pyrite are less than 2.0, and the mean ratio is 1.87. The mean ratio of S/Fe of irregular granular pyrite is 1.96, which is closest to the theoretical value.

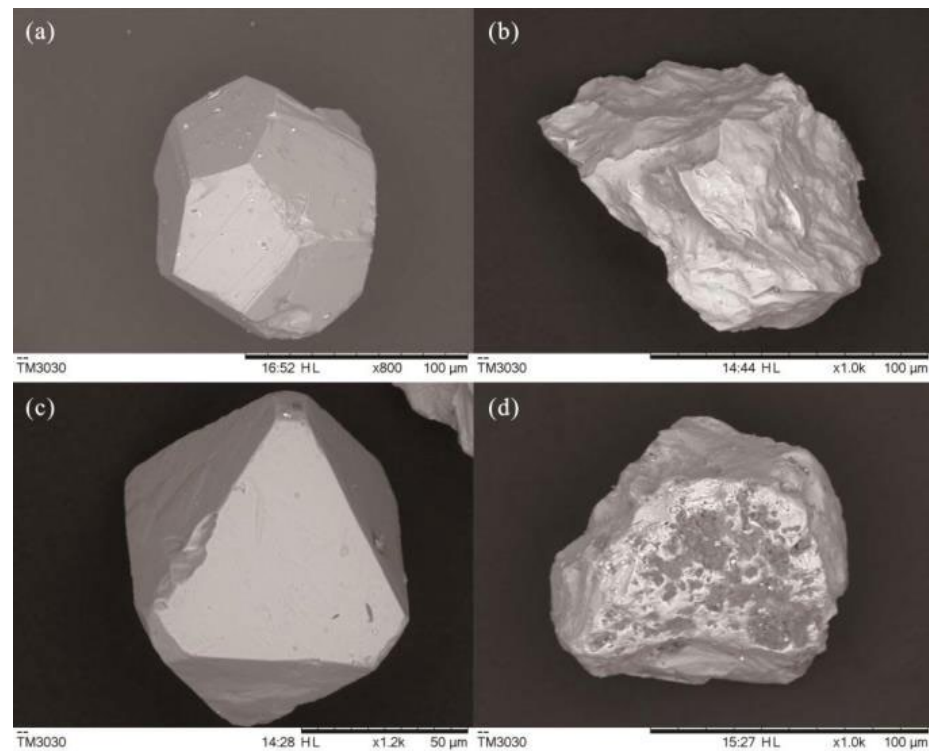


Figure 8. SEM photos of pyrite crystals in the samples of the well MK-3 in Simao Basin. (a) Sample No. P-5, typical pentagonal-dodecahedron crystals; (b) Sample No. P-8, irregular granular pyrite crystal in the sample; (c) Sample No. P-13, Typical octahedral pyrite crystals; (d) Sample No. P-12, the surface of irregularly granular pyrite shows corrosion pits.

Table 2. Crystal type, grain size, $\delta^{34}\text{S}_{\text{V-CDT}}$, and S/Fe ratio of pyrite in the well MK-3 salt formation samples from the Simao Basin.

S.N.	No.	Crystal Type	Grain Size/ μm	S/Fe	$\delta^{34}\text{S}_{\text{V-CDT}}/\text{‰}$				
					Maximum	Minimum	Mean	S.D.	M.A.
1	P-1	-	-	-	0.79	7.35	4.36	3.58	3
2	P-2	-	-	-	−2.36	6.97	1.28	3.00	15
3	P-3	I.G.	50–180	1.97	−15.65	11.41	5.7	4.90	30
4	P-4	I.G.	50–100	1.87	−3.9	11.57	6.62	3.27	30
5	P-5	P.D.	100–120	2.11	3.89	11.03	8.2	2.26	15
		I.G.	100	2.03					
6	P-6	I.G.	100–160	1.84	−3.2	7.26	3.53	3.36	15
7	P-7	P.D.	60–100	2.32	−0.82	4.47	2.25	1.36	15
8	P-8	I.G.	100–200	2.05	−3.49	8.12	4.43	2.68	30
		Cuboidal	90–120	1.89					
		P.D.	90	2.02					
9	P-9	I.G.	120–220	2.01	1.72	7.99	4.17	1.47	30
		Cuboidal	160–200	1.85					
		P.D.	90	2.27					
10	P-10	I.G.	120–300	1.98	−0.83	6.96	4.29	1.93	30
11	P-11	-	-	-	−13.74	11.81	0.79	10.30	30
12	P-12	I.G.	90–120	1.91	−2.87	6.48	2.08	2.87	30
13	P-13	Octahedral	50–100	1.87	−15.02	−6.36	−10.66	2.66	15

Note: "-" is not detected. S.N.—Sequence Number; No.—number; P.D.—pentagonal-dodecahedron; I.G.—irregular granular; S.D.—standard deviation; M.A.—measured amount.

The average $\delta^{34}\text{S}_{\text{V-CDT}}$ values of pyrite in clastic rock from the upper salt rock range from 0.79‰ to 8.20‰ (Table 2). The minimum values of $\delta^{34}\text{S}_{\text{V-CDT}}$ for pyrites of P-5 and P-10 are −15.65‰ and −13.74‰, respectively. The standard deviation of $\delta^{34}\text{S}_{\text{V-CDT}}$ of sample p-10 reached 10.30‰, indicating that the data were discrete. Further analysis showed that the data had the characteristics of "double peaks" (see Figure 9), with main peaks ranging from −13‰ to −14‰ and 10‰ to 12‰, respectively.

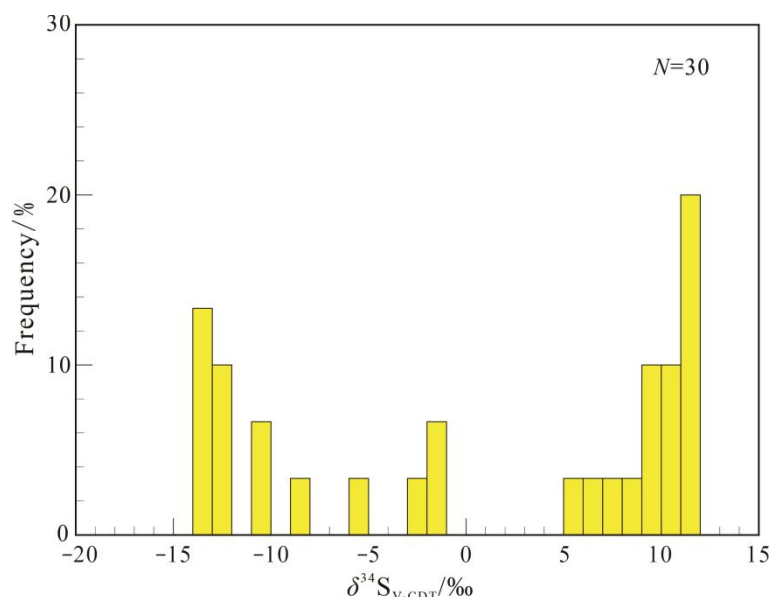


Figure 9. Distribution characteristics of $\delta^{34}\text{S}_{\text{V-CDT}}$ in pyrite of sample No. P-11, indicates that the values are very discrete and can be divided into two main peaks. One is −13‰~−14‰, and the other is 10‰~12‰.

The $\delta^{34}\text{S}_{\text{V-CDT}}$ values of pyrite in clastic rock samples between salt rocks range from −15.02‰ to −6.36‰, with a mean value of −10.66‰ and a standard deviation of 2.66‰. The $\delta^{34}\text{S}_{\text{V-CDT}}$ values are significantly different from those of pyrite samples from the upper salt layer.

5. Discussion

5.1. The Origin of Pyrite

Pyrite is the most common sulfide in the crust, widely distributed in sedimentary rocks, metamorphic rocks, and magmatite. The most common crystal forms include idiomorphic crystals, anhedral crystals, and strawberry-like aggregates [30,31].

The diameter of framboidal pyrite in sedimentary rocks is usually several microns to tens of microns, and the redox conditions of the sedimentary environment can be identified by its particle size changes [8]. The largest framboidal pyrite formed under sulfide conditions is generally less than 7 μm in diameter, while crystals up to 50 μm in oxidizing and sub-oxidizing conditions may occur [32]. Large grain single crystal pyrite or vein pyrite are mostly deposited in sediment pores in early diagenesis or formed in hydrothermal transformation in later diagenesis [31].

The petrological characteristics of the samples above the halite layer in the well MK-3 show that the detachment surface is developed along the laminae and the detachment space formed is filled with siliceous, dolomite, and calcite. In the fill, pyrite crystals exist in the form of mineral inclusions (see Figure 5). The pyrite crystals dispersed in the mudstone matrix exist in the tiny pores by observation under a microscope, and the pores not only are connected to the outside world with micro-cracks but also are filled by dolomite or calcite (see Figure 7c–f). The morphologic characteristics of the pyrite crystals show that the particle size of pyrite crystals is between 50 and 300 μm , which is larger than that of the

sedimentary pyrite crystals. The crystal morphology is mainly pentagonal-dodecahedron, cube, and irregular granular, and no typical framboidal pyrite that can serve as an indicator of sedimentary origin has been found. According to the above characteristics, it is inferred that the pyrite in the upper part of the rock salt layer of MK-3 is of hydrothermal origin.

Mojiang gold deposit (MGD) is a hydrothermal type of gold deposit [33–36]. The perpendicular distance between the Amojiang fault and the sample exploration well MK-3 is about 20 km (see Figure 1). Theoretically, relevant hydrothermal fluid is connected to the fault system. Since the $\delta^{34}\text{S}$ value of hydrothermal pyrite is controlled by the oxygen fugacity, pH, and temperature of the hydrothermal fluid [37], it is also closely related to the sulfur source in the hydrothermal fluid [37,38]. The existing research results on sulfur isotopes of hydrothermal pyrite in MGD have important reference significance for this paper. The results show that the $\delta^{34}\text{S}_{\text{V-CDT}}$ value of hydrothermal pyrite in the MGD is -8.35‰ to 0.64‰ , with an average value of -4.45‰ , which is consistent with the $\delta^{34}\text{S}_{\text{V-CDT}}$ value of pyrite in surrounding rock (-5.1‰ to -2.9‰) [34,35].

The $\delta^{34}\text{S}_{\text{V-CDT}}$ values of the pyrite above the salt layer of the well MK-3 vary from -15.65‰ to 11.81‰ , which is larger than the variation range of $\delta^{34}\text{S}_{\text{V-CDT}}$ values of the hydrothermal fluid of MGD, indicating that the source of sulfur elements is complex. The average values of $\delta^{34}\text{S}_{\text{V-CDT}}$ of all samples are 0.79‰ to 8.20‰ , which is significantly higher than the $\delta^{34}\text{S}_{\text{V-CDT}}$ values of the hydrothermal fluids and surrounding rocks of the MGD, indicating that there is a more sulfur source with ^{34}S content in the formation of pyrite above the halite formation in the well MK-3.

There is an anhydrite layer at 2394.4 to 2396.6 m depth above the salt layer in the well MK-3, with $\delta^{34}\text{S}_{\text{V-CDT}}$ values ranging from 13.9‰ to 15.1‰ (see Figure 10) [3]. The anhydrite provides a sulfur source with heavy sulfur isotope content for pyrite through thermochemical sulfate reduction (TSR) under hydrothermal action [39]. As a result, the $\delta^{34}\text{S}_{\text{V-CDT}}$ value of pyrite in the strata located over the rock salt layer in the well MK-3 is larger than that of hydrothermal pyrite in the MGD.

Sulfate reduction involving bacteria can produce a maximum of 5.1‰ to 23.7‰ sulfur isotope fractionation [40], and a larger sulfur isotope fractionation will be generated if disproportionation occurs [41]. Therefore, the anhydrite rocks at the depth of 2394.4 to 2396.6 m in well MK-3 may also be modified by microbial reduction and provide sulfur sources with relatively low ^{34}S content during the formation of pyrite, as shown by pyrite crystals with abnormally low $\delta^{34}\text{S}_{\text{V-CDT}}$ value in samples No. P-3 and P-11.

Sample No. P-13, located between the salt layers in the well MK-3, was gray-black dolomitic mudstone with undeveloped cracks, and no pyrite was observed in the core and thin sections. In this paper, the pyrite crystals for sulfur isotope testing were obtained by gravity separation. Under an SEM, pyrite crystals are octahedral with a particle size of 50 to 100 μm . The $\delta^{34}\text{S}_{\text{V-CDT}}$ values of pyrite range from -15.02‰ to -6.36‰ with an average value of -10.66‰ . The $\delta^{34}\text{S}_{\text{V-CDT}}$ values of anhydrite with similar depth (2524.4 to 2526.1 m) range from 15.1‰ to 15.5‰ . The $\delta^{34}\text{S}_{\text{V-CDT}}$ value of anhydrite deposited in the early stage (at a depth of 2627.8 m) is 15.5‰ [3]. It is concluded that pyrite is of sedimentary origin and H_2S generated by anhydrite formed in the early biodegradation stage is an important sulfur source. The initial form of pyrite of sedimentary origin is mostly framboidal. Due to the limited stability of framboidal pyrite, it will be transformed into idiomorphic crystals with the change of occurrence environmental conditions [42,43]. For example, the sedimentary octahedral pyrite is developed in the seabed sediments of the Xisha Trough in the northern South China Sea, and its $\delta^{34}\text{S}_{\text{V-CDT}}$ value ranges from -33.49‰ to -19.88‰ , with an average of -29.4‰ [44]. In addition, according to the grain size characteristics of pyrite, it is inferred that the redox interface of the sedimentary environment is below the water–rock interface. Studies on shallow potash orebodies also show that octahedral pyrite is of sedimentary origin and can be used as a standard mineral indicating a potash salt layer [23].

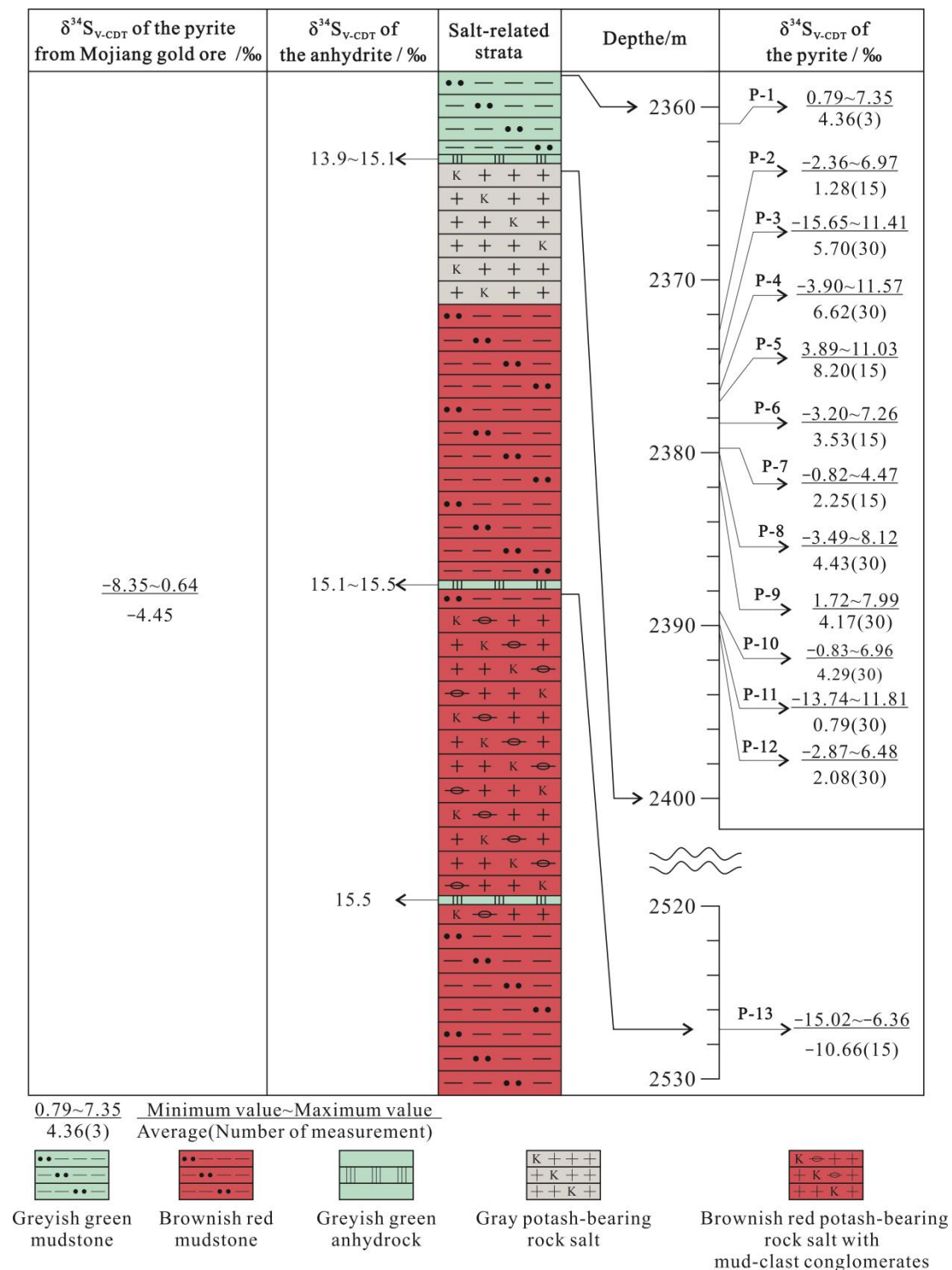


Figure 10. Distribution characteristics of $\delta^{34}\text{S}_{\text{V-CDT}}$ values of pyrite in well MK-3 salt-related strata samples and comparison with $\delta^{34}\text{S}_{\text{V-CDT}}$ values of pyrite in anhydrite and hydrothermal fluid pyrite of MGD. It can be seen that the $\delta^{34}\text{S}_{\text{V-CDT}}$ value of hydrothermal pyrite from the MK-3 well is larger than that of hydrothermal pyrite in the Mojiang gold deposit. Its sulfur source is not only hydrothermal fluid but also H_2S produced by anhydrite TSR and BSR in the formation. Moreover, TSR accounts for a large proportion, so it is represented by a large variation range of the pyrite $\delta^{34}\text{S}_{\text{V-CDT}}$ value and is generally positive.

5.2. Properties of Hydrothermal Fluids about Pyrite

The analysis of quartz fluid inclusions in the MGD shows that the salinity of hydrothermal fluid ranges from 0.1% to 14.8%, with an average of 5.48%. The main components of hydrothermal fluid are H_2O , CO_2 , Mg^{2+} , Ca^{2+} , Na^+ , K^+ , SO_4^{2-} , F^- , and Cl^- [35]. This hydrothermal fluid can provide a sufficient source for the precipitation of calcite or dolomite. However, the characteristics of the Na^+/Cl^- ratio indicate that the hydrothermal fluid has not dissolved the rock salt. The homogenization temperature of quartz fluid inclusions in the main ore-forming stage is 122 to 306 °C [45], reflecting the characteristics of medium-low temperature hydrothermal mineralization [46]. Analysis of the characteristics of hydrothermal mineral association shows that there are three phases of hydrothermal activity, and the mineral association of the third phase of hydrothermal activity is calcite, quartz, and pyrite, and the hydrothermal temperature drops to 98~180 °C [46]. According to geochronological studies, the main body of hydrothermal activity consists of two periods, namely the middle to end Yanshanian and the Himalayan period [47,48].

The mineral association of hydrothermal pyrite in the well MK-3 is carbonate-quartz-pyrite, which is the same as the mineral association of hydrothermal activity in the third stage of the MGD. The crystal morphology of pyrite can reflect further metastable iron sulfides supersaturation or temperature conditions. With increasing supersaturation, pyrite morphology changes in the following order: cube + pentagonal-dodecahedral + octahedron + spherulite [49]. The usually high- or low-temperature hydrothermal fluids are easy to form cube pyrite, and medium-temperature condition is easy to form pentagonal-dodecahedral pyrite [7,50]. At low temperatures, pyrite crystals with lattice defects are more easily formed [9]. A large number of pentagonal-dodecahedral crystals and a small number of the cube and irregular granular crystals appear in the pyrite of the well MK-3. This indicates that the content of metastable iron sulfides in the hydrothermal is low and the temperature condition is medium-low range. These characteristics are similar to the properties of the hydrothermal fluid of MGD.

Generally, a S/Fe ratio less than 2 is called a sulfur deficit, and a S/Fe ratio greater than 2 is called an iron deficit [51]. The change of the S/Fe ratio of hydrothermal pyrite in the salt-related layer of the well MK-3 shows that the pentagonal-dodecahedral pyrite is precipitated when the iron is deficit, and the cuboidal pyrite is precipitated when sulfur is deficit, and the irregular granulous pyrite is precipitated when both Fe and S are not deficit. This indicates that the relative contents of sulfur and iron in the hydrothermal fluid are also changing even in the same phase, which will affect the crystal morphology of pyrite precipitation.

5.3. Influence of Hydrothermal Activity on Potash Mineralization

The core of the deep potash-rich body revealed by the well MK-3 is intact, and the sedimentary rhythm is clear. The main mineral components were identified as halite, sylvite, anhydrite, and clay minerals under the polarizing microscope. The evidence of hydrothermal influence on potash mineralization has not been found.

Hydrothermal activity has an obvious influence on MPD. It is manifested in that (1) the mineral composition of the ore contains typical hydrothermal mineral "tachyhydrite" [19]. (2) Pyrite rich in cobalt and nickel exists in the rock salt, and the cracks in the salt bed are filled with cobalt-nickel-containing combainite [52]. (3) The content of heavy metals in vein potash is significantly higher than that in layered potash and other evaporative basins in the world, which may be caused by the dissolution of previously bedded potash orebodies by hydrothermal fluid [53]. (4) Malachite and azurite are distributed in fractures [52]. (5) Rubidium (Rb)-Sr isotope characteristics show that hydrothermal activities that have been regulating and reforming the MPD occurred from the middle Miocene to the present [27]. It can be seen that hydrothermal fluid began to affect shallow potash mineralization from the evaporation and precipitation of potash. This kind of influence can not only bring a deep source to the potash deposit, make the chemical composition of the

formed more complex, but also have the dissolution transformation effect on the already formed potash deposit.

6. Conclusions

This paper aims to reveal the origin of pyrite in deep salt-related strata in the Simao Basin and its influence on potash mineralization. Optical microscopes, SEM, EDS, and XRD have been used to analyze the petrology of the clastic rock in the salt-related strata and the occurrence state, morphology, and grain size of the pyrite crystal. LA-MC-ICP-MS has been used to analyze the sulfur isotope of the pyrite in situ. We have completed a comparative study of pyrite with the hydrothermal genesis of the MGP.

Based on the above work, the findings obtained are shown as follows:

The pyrite from deep salt-related strata is of hydrothermal genesis, in the Simao Basin.

The associated minerals of pyrite in the salt-related strata are calcite and quartz. This situation indicates that the hydrothermal characteristics of the study area have been similar to the third-period hydrothermal fluid of the MGP.

The difference in sulfur isotope between single pyrite crystals is large; the minimum value of $\delta^{34}\text{S}_{\text{V-CDT}}$ is -15.65% ; and the maximum value of $\delta^{34}\text{S}_{\text{V-CDT}}$ is 11.81% . These values reflect differences in sulfur sources.

The sulfur source of the pyrite characterized by the heavy sulfur isotope is from TSR, and the sulfur source of the pyrite characterized by the light sulfur isotope is from BSR.

At present, it has not been found that deep salt bodies in the study area are affected by hydrothermal activities. However, multiple pieces of evidence support that the MPD was affected by hydrothermal activity since the beginning of the mineralization period.

Furthermore, we deduct that the sulfur source of hydrothermal genesis pyrite in the study area has been more strongly influenced by evaporite than that of the MGD, because the spatial location of the well MK-3 is closer to the salt-precipitation basin center. The pyrite from the clastic interlayer between rock salt is of sedimentary origin, and its sulfur source is from BSR. The sedimentary environment of the clastic rock is from oxidation-weak to oxidation condition, and the redox interface is below the water–sediment interface.

Our research not only reveals that the hydrothermal activity has occurred after deep potash-bearing salt precipitation but also discovers differences in sulfur source in the hydrothermal fluid, and this difference may imply that the composition, temperature, and pressure of the hydrothermal fluid is characterized by undulation.

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