Characteristic Sulfat Geochemistry of Barite (BaSO4) Marine Type on Marl Tonasa Formation Barru, South Sulawesi

A Tonggiroh1*, M Farida1, H Sirajuddin1 and D P Battu

Department of Geology, Engineering Faculty, Hasanuddin University, Makassar, Indonesia

*E-mail: adi_unhas@yahoo.com

Abstract. Barites can form in the marine environment as autogenic minerals, which are dominated by barium, carbonate and sulfate elements. Barite mineral distribution on Marl are occurred on two location which are Ralla and Barru Area (1) Ralla, irregular shape (2) Barru, barite concentration, slightly rounded. The study aims to determine sulfat geochemistry as chemical bond and the influence of barium depositional environment. Applied Petrography, SEM and XRD Analysi on Marl, Andesite, and Barite mineral. Tabular rosset texture with minor Calcite are indicated that source of Sulfat material comes from Neritic environment (Barru) and penetration of hydrothermal solution.

1. Introduction

Barite is autogenic sediment mineral [1] formed by chemical mixing of unsaturated seawater (Ba2+) dan (SO42-) deposited or filled in cavity of hydrothermal rocks [2]. The chemical structure of barite is slightly simple and processing to obtain economically value through extracted of separat ion between sulfate and clay. Barite (BaSO4) is mostly contain barium formed by various low temperature and pressure (25 °C, 1 atm) and very low solubility [3].

Chemical and physical properties of barite are common reason this minerals are used in various industries such as : (1) lubricating and solid material at drilling oil and gas industry to increase hydrostatic pressure (2) medical equipment industry; X-RAY filter in the field of radiology (3) mixture on plastic industry, rubber sludge, (4) automotive, clutch bearings, car sound absorbers, brake pads (5) electronic, radiation shield for television and computer (6) golf ball (7) paint industry(8) glass industry (9) mold coating, easily release of material from the mold.

Barium sulfat is formed from chemical mechanism of mixing interaction between dominated Ba solution and SO4 as deposition material on shore and marine environment [3, 4].

Barite as marine deposition, characterized by occurrence on lithology with relative high calcium contain such as calcareous clay/marl, recognized on research area as nodul fragment concression on marl layer of Tonasa Formation (Figure 1).

Research was held by LBE (Labo Based Education) Program, Engineering Faculty of Hasanuddin University to analysis sulfat geochemistry that occurred as Barium element on Barite mineral that correlated with Sulphide Alteration Mineralization on Dacite igneous rock.
2. Regional Geology

Research area regional include on Tonasa Formation that formed by intercalation between Limestone and Marl abundant of fossil lies on Barru Area and Limestone contain with schis fragment and ultramfic occurred at Ralla Area (Figure 2). Tonasa Formation consist of marl with limestone as member, neritic environment depositional, Miosen age.

![Figure 2. Regional Geology [5], research area Ralla and Barru](image)
Abundantly of macro and micro foraminifera, shown if Tonasa Formation range Early Eosen (Ta.2) to Middle Miosen (Tf). Relative age of marl and limestone is Early Eosen to Late Eosen (P9-P16). Cycle of depositional environment between Inner Neritic-Middle Neritic-Outer Neritic occurred during sedimentation, medium water temperature (range 35°C), salinity on marine lagoon and carbonate platform [5].

3. Method
Barite mineral sample (ADB01; ADR02) convert to thin section with 0.8 – 1.2 cm thickness, SEM-EDX (Scanning Electron Microphobe-Emision Diffraction X-ray) Jeol-JSM 6610LV, Mineral Resources Laboratory Akita University (Figure 3).

Determined barium contain on Iodin solution 50 ml (0.5 N) and 1N hydrochlorid acid, followed by agglomeration and titration, conducted at Chemical Laboratory Engineering Faculty Unhas.

Igneous rock sample (ADB 03; ADB04), convert into thin section with thickness 1.0 cm polished till 0.03 and 0.05 mm thickness than observed under polarization microscope on Optical Mineral Laboratory of Technical Faculty of Hasanuddin University.

Figure 3. SEM EDX Jeol-JSM 6610LV

4. Field Situation
Research area is located on Barru and Ralla District Barru Regency South Sulawesi Province coordinate 119°37'00"–119°38'00"; 119°41'00"–119°42'00" East Longitude and 04°25'00"–04°26'00" South Latitude.

Field orientation shown if barite deposited has white clear brownish, rosset tabular structure, kohesif, slightly heavy and rounded with diameter < 6 cm, found as infiltration nodule on marl at Barru and slightly irregular shape at Ralla.

Intercalation between marl and limestone was shown changing on depositional environment that relative southwest – Northeast or from Barru to Ralla (Figure 4). Geological structure was developed as Normal Fault on marl with Middle Eocen – Post Middle Miocen.
5. Lithology

Field interpretation shown two outcrops were founded on research area; Andesite and Marl. Macroscopic description recognized blackish intercalation limestone on Marl, bioclastic texture and layering (Figure 5).

Marl megascopic description (AD01) grey, brownish grey, fine clastic, good sortation, fabric, silt to clay grain size and calcareous. Microscopic analysis shown; yellow brownish absorb color, brown interferen color, clastic with fossil (62%), micro foraminifera (Globigerina sp), calcite (20%), pore (3%), mud supported (15%), 

Grainstone.

Limestone megascopic description (AD02) brown absorb, brown reddish interference, bioclastic texture with grain (35%), foraminifera fossil Actinocyclina radians (d’Archiac) and Dyscocyclina pratti (Michelin) and Alga (15%); Grain non skeletal litoclas (5%), sparite (10%), carbonate mikrit (35%), 

Packstone (Figure 6).
Andesite (AD03), grey, brownish grey, medium prophylitic alteration, patchy feldspar with pyrite lineation on oxide cracking (Figure 7).

Microscopic description, white greyish brown, hypocrystalline, porfiritic, (Fenokris 40% ; Glass 60%), hyalopilitc, mikrolite feldspar subparalel on glass mineral. Fenokris Sanidine, plagioclase, feldspatoid, biotite and Hornblend (50 – 500 μm), euhedral - anhedral, Trachyte Andesite.

Field description dacite (AD04), grey to brown blackish, hypocrystaline, porfiritic, euhedral-subhedral, inequigranular, and masif. Composition mineral plagioclase, quartz, hornblende, and glass.

Figure 6. Thin section 50x, fragment : (a) grainstone (b) packstone

Figure 7. Thin Section 50x, (a,b) trachyte andesite

Mikroscopic, brown absorb color with grey blackish maximum interference, hipocrystalline, faneroporftitic, euhedral-subhedral, inequigranular, labradorit (35 - 40%) occasionally change to sericite, hornblende (15 - 20%) occasionally change to chlorite, quartz (10 – 15%), groundmass plagioclase crystalline (20 – 25%), groundmass as glass mineral (10 – 15%), indeks warna 20, Dasit Porfiri (Travis, 1955).

6. Barite Petrogrpahy

Petrography analysis for sample AD_05 shown if mostly barite mineral has transparent absorption, size (0,1 sampai 2,6 mm); calcite rhombohedral, size (0,1 sampai 0,875 mm), plaktonik fosil microcrystalline (0,125 sampai 2,75 mm). Orthorombic structure form pinacoid block, prismatic that contain with clay micrite and sronsium (Sr) minor (Figure 8).
Figure 8. Thin section 50x, mineral barit

Based on carbonate composition, microcrystalline and micrite, indicated if barite was deposited on lower part of Marl marine sedimentation; deep-sea marine with abundant of calcareous dan siliceous biological debris.

7. Crystal Chemistry

Barite has orthorhombic dipirimaldial crystal structure, one sulfur bond and two-oxygen bond as sulfat (SO$_4^{2-}$) tetrahedron [6]. Sulfur has chemical substitution affected by chemistry of depositional environment and hydrothermal solution. Number of sulfur and barium are linier as chemical reaction on environmental deposition (Table1).

| Sample ID | Ba (%) | S (%) | Si (%) |
|-----------|--------|-------|--------|
| AD05      | 72.04  | 20.67 | -      |
| AD06      | 67.16  | 13.46 | -      |
| AD07      | 51.49  | 14.28 | 5.68   |
| AD08      | 54.76  | 16.52 | 0.41   |
| AD09      | 40.39  | 11.39 | 12.5   |
| AD10      | 68.92  | 16.19 | -      |

Minimum S (40,39; 11,39) and maximum (72,04; 20,67) are the hypothesis explain dominated Ba than S. Indicated if depositional environment of barite was dominantly effected by marine than shore sedimentation (Figure 9).

On marine environment, substitution Ba$^{2+}$ occurred as ion radius and anion of Sr$^{2+}$ dan Ca$^{2+}$ on particle phase with other element such as carbonate, organic, oval, ferromanganese hydroxide, mainly exist on marine and terrestrial environment that contain of silicate of detrital environment.
8. Discussion
According dominated of barium element (Ba), less number of sulfat and petrography analysis are shown the characterized of sedimentation process such as deposition, diagenetic and erosional to build texture and shape of lithology. During diagenetic process, mud material is fill into the cavity of barite, thus precipitation of marl formed the angular prismatic crystal as erosion effect. Occurrence of micrite and plactonic are shown condition wet paleoclimate where clay depositional exist on marine environment. Uneven distribution of silica on few samples and less number of sulfat are need further research as part of mixing system either hydrothermal or erosion of continent element.

References
[1] Boggs JR, 2009, Petrology of Sedimentary Rocks, Cambridge University Press, p.6.
[2] Ehya, F, Mazraei SM., 2017, Hydrothermal barite mineralization at Chenarvardeh deposit, Markazi Province, Iran: Evidences from REE geochemistry and fluid inclusions, Journal of African Earth Sciences, 134, p.299-307.
[3] Church TM, Wolgemuth K, 1972, Marine barite saturation, Earth and Planetary Science Letters, V.15, Issue 1, p.35-44.
[4] Griffith, E.M., Paytan, A., 2012. Barite in the ocean-occurrence, geochemistry and palaeoceanographic applications. Sedimentology 59, 1817-1835.
[5] Jaya, A, Nishikawa, Osamu, Hayasaka, Yasutaka, 2017, LA-ICP-MS Zircon U–Pb and Muscovite K-Ar Ages of Basement Rocks from the South Arm of Sulawesi, Indonesia, Lithos.
[6] Dana, 1977, Manual of Mineralogy, John Wiley & Sons, p.317.