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The nature of ultramafic rocks from Sulawesi, Indonesia and their suitability for CO₂ sequestration

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Abstract. Petrological and geochemical characterization of some ultramafic rock samples from Sulawesi has been conducted with the aim at deciphering physico-chemical properties in relation to their potential use as carbon dioxide storage. Mineralogical analysis was performed by means of optical microscopy and whole rock chemical compositions of the samples were determined by X-ray fluorescence (XRF) spectrometry. Results of analyses show that lizardite is predominant serpentine mineral present, followed by chrysotile and trace amount of magnetite. Remnants of olivine and pyroxene were detected in some samples but they have been pseudomorphically replaced by serpentine. Serpentinization of Sulawesi ultramafic rocks has led to transformation of olivine and lesser pyroxene become secondary phases mainly lizardite and minor chrysotile. This process also has changed the properties of rocks such as reduction in grain size and decreasing in density. Relatively higher MgO concentration combined with fine grained and porous rocks indicate that some Sulawesi ultramafic rocks are good candidate as the host for mineral carbonation. Fosteritic olivine and serpentine (lizardite) are the most soluble Mg-rich minerals in acid. Carbonation may occurs where Mg²⁺ readily reacts with CO₂ forming thermodynamically stable magnesite (MgCO₃)

1. Introduction

The increase of fossil fuel combustion use in various industrialization as the main source of energy, have negative effect due to a large amounts of CO₂ released into the atmosphere [1]. These have led to enhance the global temperature which is known as global warming. In order to overcome this, it is important to look for the effective ways in diminish the quantities of CO₂ escaped into atmosphere. Total global CO₂ emissions in 2016 reached up to 49.3 gigatonnes with China, USA, India, Russia and Japan are the five largest emitting countries [2]. Indonesia contributes to about 0.53 gigatonnes of global CO₂ emissions which are mainly derived from coal fire power plant, cement factory, metallurgical plant and other industrial processes.

Subtraction of CO₂ emission can be partly coped with by capturing it from the point sources, separating it from flue gas and disposing it into the geological reservoirs which is known as CO₂ sequestration. There are three different methods that can be applied to sequester CO₂ into geological



formation (i.e. hydrodynamic, solubility, and mineral trapping) [3]. Hydrodynamic sequestration involves the trapping of CO₂ gas as supercritical fluid in sedimentary strata which are underlined by a cap rock or impermeable layer [4]. Solubility trapping is a technique to dissolve CO₂ gas with formation water forming aqueous compounds such as H₂CO₃⁰, HCO₃⁻ and CO₃⁻². Mineral trapping includes the reaction of CO₂ gas with Mg- and Ca-rich minerals forming new more stable carbonate phases.

Ultramafic rocks are widely distributed in Sulawesi which can be found in Barru, Pangkep, Malili, Soroako, and some other localities in east and central Sulawesi [5,6]. These rocks might be good candidate materials for mineral carbonation. The primary objective of this study was to characterize the mineralogy and bulk rock chemical composition of ultramafic rock samples from some localities in Sulawesi and their suitability as feed material for CO₂ sequestration.

2. Mineral Carbonation Technology

Mineral carbonation (MC) is one of alternative method for carbon dioxide disposal. It was introduced for the first time by Seifritz [7]. This method is assumed to be more efficient way in sequestering CO₂ because the formed carbonates are thermodynamically stable over the long time [8]. The reaction is also exothermic so that it does not need additional input energy. Carbonation option in ultramafic rocks are promising due to the rocks containing significant reactive minerals mainly olivine and serpentine. Two options of MC technology are currently recognized (e.g. *in situ* and *ex situ*). *In situ* mineral carbonation involves the injection of CO₂ into subsurface reservoirs to enhance the reaction of CO₂ with Mg-Ca-bearing minerals present in the geological formation. *Ex situ* mineral carbonation is performed above ground in an industrial plant using pre-existing rock mining materials [9,10,11]. *Ex situ* is further divided into direct carbonation (DC) and indirect carbonation. Direct carbonation consists of gas-solid carbonation and aqueous carbonation; whereas indirect carbonation involves the first extraction of reactive elements (Mg or Ca) in one step, followed by reaction leached cation with CO₂ in subsequent step to produce the desired carbonate minerals. Production of stable carbonate phases may take place through reaction between CO₂ and alkaline earth as following equation:

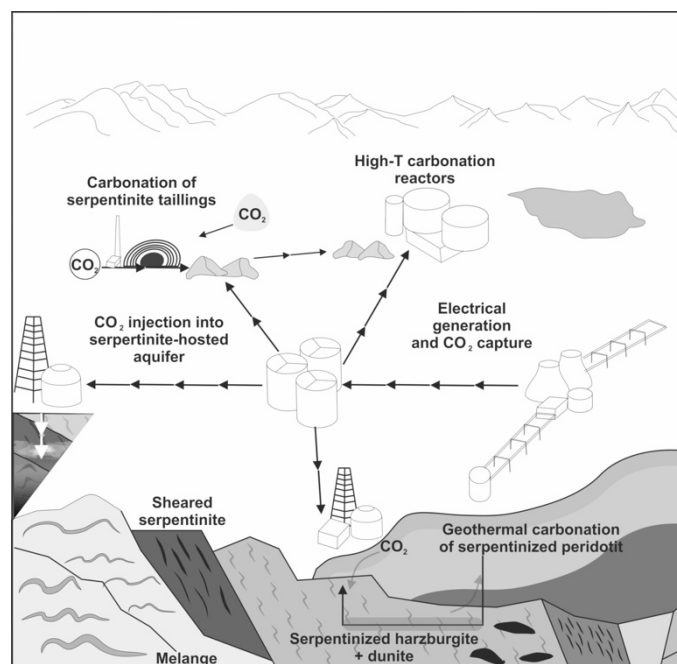
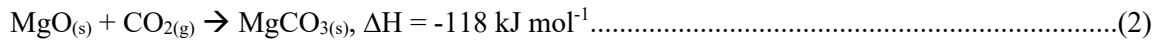
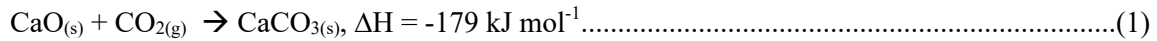


Figure 1. Schematic diagram depicting the options of mineral carbonation technology [9].



3. Samples and Methods

Ten ultramafic rock samples use in the present study were collected from five different localities in Sulawesi (Figure 2). Mineralogical obervation of samples was carried out under polished- thin sections using optical polarizing microscope (Nikon; Eclipse-LV100) either on refraction or reflection mode.

Representative rock samples were crushed by means of jaw crusher followed by manual grinding using agate mortar in order to produce powder materials. About two grams of such powder samples were put into PVC rings to make press pellet prior to be submitted to XRF analysis. This analysis was applied to determine the major oxides and some trace element content of the samples. Detection limit of major oxides is 0.01 wt% and trace elements is 10 ppm for Cr, Ni and Co; wheras 4 ppm for V.

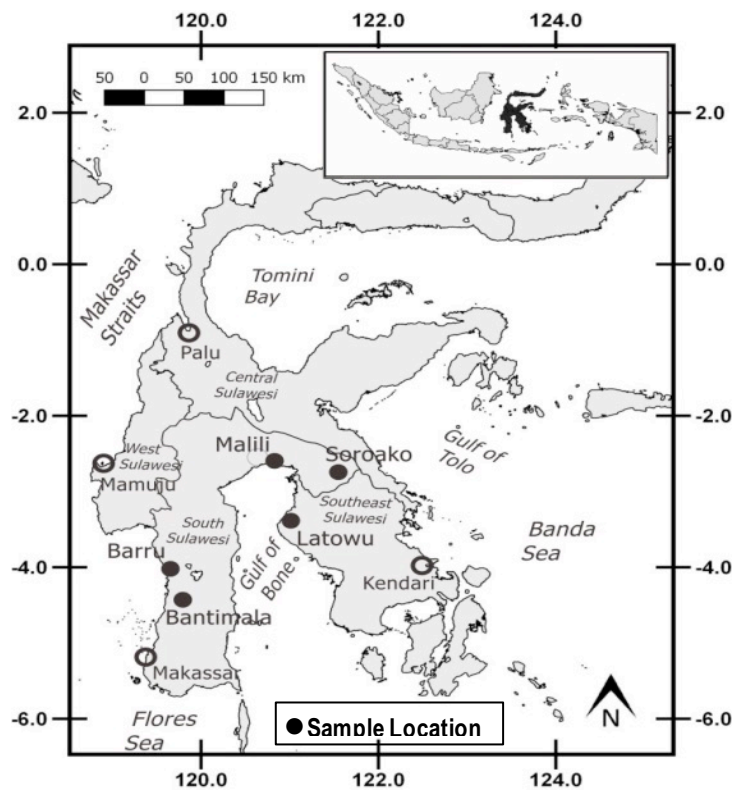


Figure 2. Map showing sample localities of ultramafic rock use in this study

4. Results and Discussions

4.1 Petrology and Mineralogy

Summaries of petrographic features of representative ultramafic rocks from Sulawesi are presented in Table 1. The ultramafic rocks in the Soroako are largely harburgite with locally dunite. Typical ultramafic rocks of Soroako West Block, however, are clearly different from Petea Block due to their serpentinization degree. The wes block is charcaterized by highly fractured with very low to unserpentinized ultramafic. The modal mineralogy consist of medium to coarse grained olivine (75-95 vol%), orthopyroxene (up to 14 vol%), small amount clinopyroxene and trace spinel (Fig. 3A & 3B).

Table 1. General descriptions of ultramafic samples used in this study

Sample	Locality	Rock Type	Serp. Degree	General Description
IN-01	Soroako West Block	Harzburgite	<2 %	Light green to grey, medium grained, massive, an. OL with 0.05 – 1 mm (80%) OPX (14 %), CPX (5%), and spl (1%).
AN-03	Soroako West Block	Dunite	<5 %	Light to med. green, coarse to med. grained OL (~95 %), OPX (~2 %), spinel (~3 %).
PB-04	Petea Block	Harzburgite	~50%	Med. brown, serpentine (50 %), locally OL remnants (~23 %), the OPX (~20%) and CPX (5 %), trace magnetite (~2%).
PB-06	Petea Block	Dunite	>90 %	Fine grained texture, srp (90 %), OPX bastite (~5 %), relic OL (~2 %). Trace mag. (up to 3%). The original mode estimated at 95 % olivine and 5 % OPX.
SU-5A	Malili Area	Harzburgite	>60 %	Light brown, fine grain, srp (60 %), OL remnants (~20 %), OPX (~15%) and CPX (5 %), trace magnetite (~3%).
SU-17	Malili Area	Harzburgite	>70 %	Med brown, fine grain, srp (~70%), OL relic (~15%) OPX (~10%), CPX (~2%), mag (~3%).
LT-04	Latowu Block	Harzburgite	>75 %	Light brown, fine grain, srp(~75%), OL remnant (~10%), OPX (~10%), CPX (~3%), mag (~2%)
LT-12	Latowu Block	Dunite	>90 %	Dark brown, v.f. grain, srp (~90%), OL relic (~5%), mag (~5%).
MOR-2	Bantimala	Harzburgite	~50 %	Fine grain, srp (~45%), chl (~10%), OL relic (15%), OPX (~10%), CPX (~5%), mag (~5%).
DNG-1	Barru	Harzburgite	~70 %	Med. Brown, fine grain, Srp (65%), chl (5%), OL relic (~10%), OPX (~12%), CPX (~5%), mag (~3%).

In contrast, the ultramafic rocks in the Petea Block are strongly serpentinized with degree up to 90 % by volume (Fig. 3C). Pseudomorphic replacement textures are easily observed in which olivine altered to serpentine network (mesh) and pyroxene changed to serpentine bastite.

The observation of ultramafic rock from Malili area under cross polarized displays medium brown with fine grained texture (Fig. 3D). Mostly primary phases (olivine and pyroxene) have been altered to serpentine with degree about 60 to > 70 vol%. The early phase of serpentines are penetrated by a late phase (non pseudomorphic) serpentine vein. Similar feature is shown in the ultramafic rock from Latowu area (Fig. 3E). Mostly olivines have been replaced by serpentine forming network (mesh texture), although some olivine relics can still be seen. Alteration of pyroxene into serpentine in the Latowu can also be observed which is characterized by preservation of the original crystal shapes. The ultramafic rock from Bantimala and Barru also display moderately to strongly serpentinized, however, small amounts of chlorite were detected following serpentine (Fig. 3F). This imply that serpentinization process may have been taken place in relatively higher temperature and pressure.

The presence of magnetites in all analyzed samples, with exception of Soroako west Block, indicate that serpentinization has more prone to take place at the system with very low silica activities [12]. Magnetite is not stable in the system with higher silica where serpentine minerals may be more iron-rich [13]. During serpentinization, hydrolysis of olivine was accompanied by redox process there by the Fe^{2+} was oxidized into Fe^{3+} and reduction of Fe^{2+} into Fe^0 [14]. Iron expelled from olivine structures may react with oxygen to form magnetite at oxydized condition or to form native iron at reduced condition. It is also can enter the structure of serpentine.

The oxygen required for magnetite precipitation might be extracted from decomposition of water. It is therefore inferred that the higher SiO_2 concentration of pyroxene-bearing rocks (e.g harzburgite) should contain more magnetite than those of lower SiO_2 concentration of olivine-rich ultramafic rocks (e.g dunite) because solubility of Si in serpentine mainly lizardite is greather than that of Fe^{3+} [15]. The additional Si would combine with brucite to form lizardite and liberate Fe to form magnetie. Formation of magnetite in silicates is the main cause of the reduced condition.

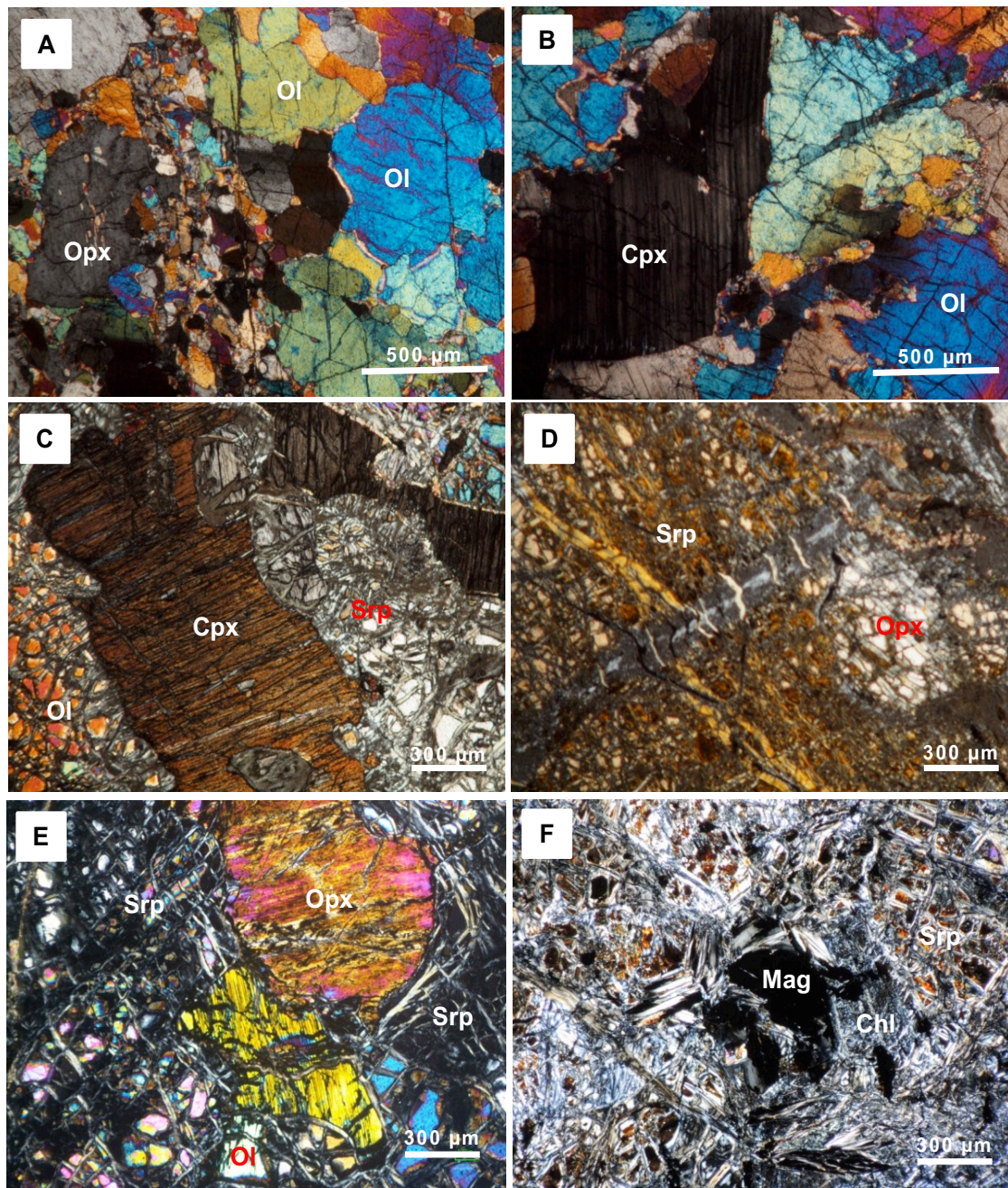


Figure 3. Photomicrographs of selected ultramafic rock (UR) samples from different localities in Sulawesi. All views under cross polarized light. A and B are typical UR from Soroako West Block showing predominantly olivine crystals and minor pyroxene. C is microscopic feature of UR from petea Block displaying strongly serpentinized with pseudomorphic replacement texture and D is microscopic appearance of a Malili sample depicting primary mesh and bastite which have been cross cut by late phase serpentine vein. E is microscopic view of UR from Latowu and F is the microscopic appearance of representative UR from Barru.

4.2 Whole-Rock Geochemistry

Results of whole-rock chemical analysis of ultramafic rocks five different localities in Sulawesi are provided in Table 2. It is shown that all studied samples have SiO₂ concentration ranging from 38.73 to

44.85 wt%. Unserpentinized harzburgite from Soroako west block contain highest SiO₂ value. Dunite from Soroako west block shows highest MgO concentration (50.43 wt%) and sample from Bantimala has lowest MgO content (34.23 wt%). Relative depletions of these major elements in Petea, Malili, Latowu, Barru and Bantimala are the consequence of water introduction during serpentinization. This process has caused reduction of MgO in serpentinized ultramafic rock samples, indicating that magnesium has been leached out in more intensive than silica. The moisture content of serpentinized samples from Petea, Malili, Latowu and Bantimala-Barru show the value from 7.08 to 13.60 wt% indicating moderately to strongly serpentinized protolith. Theoretical value of moisture content of the completely serpentinized rocks would be ~13 wt%. The highest value of MgO/SiO₂ ratio is found in Soroako west block sample; whereas the lower value is in Bantimala sample. Other important major oxide includes FeO having the maximum value in harzburgite sample from Soroako west block and the minimum value is found in Malili sample. With exception of Bantimala and Barru samples, the concentration of Al₂O₃ show lower value (<1 wt%). TiO₂ and MnO generally have lower concentration in all analyzed samples. Similarly, CaO is also generally low, around 2 wt% or less.

Chromium concentration in all studied samples has wide range variation in between 384 and 3455 ppm. The highest value is found in Soroako west block; whereas lowest value is in the Latowu block. Nickel and cobalt show higher concentration in Soroako west block followed by Petea and Malili samples. Relatively higher Ni content of Soroako west block samples reflects the domination of forsteritic olivine which theoretically has Ni concentration up to 0.5 wt%. Vanadium has lowest grade over the other trace elements considered, but it seem likely elevated value in the Bantimala and Barru samples.

Table 2. Bulk rock chemical composition of ultramafic rock samples from various localities in Sulawesi

Locality/ Sample No.	Detec. Limit	Soroako west block		Petea Block		Malili Area		Latowu Block		Bantimala-Barru	
		INA-1	AN-3	PB-04	PB-06	SU- 5A	SU-17	LT-04	LT-12	BTM- 2	BRU-1
SiO ₂ (wt%)	0.01	44.85	40.04	42.37	40.14	42.13	39.84	39.52	38.73	40.18	40.53
TiO ₂	0.01	0.01	<0.01	0.01	0.01	0.01	0.01	0.01	<0.01	0.03	0.09
Al ₂ O ₃	0.01	0.63	0.12	0.82	0.58	0.96	0.53	0.83	0.14	1.36	2.75
FeO	0.01	9.01	7.67	7.85	7.33	5.68	7.84	8.37	8.65	8.46	8.18
MgO	0.01	42.99	50.43	38.14	39.43	38.82	43.22	38.05	38.07	37.84	34.23
K ₂ O	0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.11	0.03	0.02	0.02
Na ₂ O	0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	<0.01	<0.01	0.01	0.08
CaO	0.01	0.65	0.13	1.00	0.83	0.07	0.76	0.43	0.09	1.26	2.13
MnO	0.01	0.14	0.11	0.12	0.12	0.08	0.12	0.04	0.01	0.01	0.17
LOI		0.95	0.58	9.07	10.97	11.76	7.08	11.20	13.60	10.42	12.27
Total		99.23	99.08	99.38	99.41	99.50	99.80	98.50	99.32	99.70	100.45
Cr (ppm)	10	3455	2850	3025	2755	446	2634	2209	384	3220	2573
Co	10	126	125	105	97	68	101	110	105	<10	<10
Ni	10	3402	3100	2440	2288	3630	2604	2177	2187	2137	2118
V	5	23	15	38	39	8	25	35	4	74.8	91.8
MgO/SiO ₂		0.96	1.26	0.90	0.98	0.92	1.08	0.96	0.98	0.94	0.84

4.3 Suitability for CO₂ Sequestration

With respect to CO₂ sequestration, it is shown that magnesium is the primary target of reactive element if mineral carbonation will be considered. However, other rocks properties such mineral composition and texture are also thought to have influence in the efficiency of carbonation process. The higher forsteritic olivine of ultramafic rock in the Soroako west block is desirable for ex situ option because this mineral is very reactive and contain high Mg. However the rock shows impermeable and blocky, so that it is likely not good for in situ carbonation due to high potential of leakage.

Hydration of ultramafic rocks in Petea, Malili and Latowu has caused the alteration of primary phases into serpentine mainly lizardite. This proses has also led to reduction in grain size and density of the rock. Those properties are advantageous in terms of mineral carbonation because they can promote reaction rate. In the case of ultramafic rocks from Bantimala and Barru, it is indicated that the presence of chlorite, antigorite and significant amount of spinel may hamper reaction rate. Therefore, such rocks are less beneficial as material for mineral carbonation.

In terms of petrological and geochemical perspective, ultramafic rocks from Soroako west block are favorable for ex situ option; whereas ultramafic rocks from Petea, Malili and Latowu are likely good candidate materials for both ex situ and in situ mineral carbonation.

5. Conclusion

This work present petrological and geochemical assessment of ultramafic rocks from some localities in Sulawesi and their relation to mineral carbonation. Results demonstrate that unserpen-tinized ultramafic rocks from Soroako west block are likely appropriate as raw materials of the ex situ mineral carbonation technology; whilst serpen-tinized ultramafic rocks from Petea, Malili, and Latowu are likely suitable either in situ ore ex situ methods. In contrast, ultramafic rock samples from Bantimala and Barru exhibit unsatisfactory as feedstock for CO₂ sequestration.

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