Research Article

Geochemical study of ultramafic rocks from Latowu area of North Kolaka, Southeast Sulawesi and its implication for CO_2 sequestration

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Abstract: Geochemistry of ultramafic rocks in the Latowu Area of North Kolaka Regency, Southeast Sulawesi has been investigated with the aim at deciphering of mineral characteristics, chemical composition and their potential use as carbon dioxide storage. Mineralogy was characterized by both scanning electron microscopy (SEM) and X-ray diffractometry (XRD); whereas bulk rock and mineral chemistry were analyzed by means of X-ray fluorescence spectrometry (XRF) and Electron probe microanalyzer (EPMA) respectively. 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 pseudomorphicly replaced by serpentine. Serpentinization of Latowu ultramafic rocks has led to decrease in grain size and density. Lizardite is characterized by fine grained particles with higher in iron. The higher Mg and Fe of the rocks indicate a suitability as feed materials for carbon dioxide sequestration. Mineral and chemical properties of ultramafic rocks have significant role in evaluating the feasibility of mineral carbonation.

Keywords: carbon dioxide, sequestration, serpentine, Sulawesi, ultramafic rocks
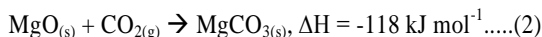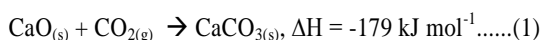
Introduction

Steadily increase of CO_2 concentration in atmosphere untill recently are mainly evoked by different anthropogenic activities such as fossil fuel ignition and other industrialization (Tahirkheli et al., 2012). These have led to elevate the global temperature which one factor in triggering the climate change. In order to mitigate the global warming, it is imperative to carry out the effective ways in reduction the amount of CO_2 released into atmosphere. Total global CO_2 emissions in 2016 reached up to 49.3 gigatonnes with China, USA, India, Russia and Japan are the five largest emitting countries (Olivier et al., 2017). Indonesia contributes to about 0.53 gigatonnes of global CO_2 emissions which are mainly derived from coal fire power plant, cement factory and other industrial process. Mitigation of CO_2 emission can be partly resolved by capturing it from the point sources, separating it from flue gas and disposing it into the geological reservoirs which is known as CO_2 sequestration. There are three different methods that can be applied to sequester CO_2 into geological formation (i.e. hydrodynamic, solubility, and mineral trapping), (Mani et al., 2008). Hydrodynamic sequestration involves the trapping of CO_2 gas as supercritical fluid in sedimentary strata which are underlined by a cap rock or impermeable layer (Kharaka et al., 2013). Solubility trapping is a technique to dissolve CO_2 gas with formation water forming

aqueous compounds such as $H_2CO_3^o$, HCO_3^- and CO_3^{-2}. Mineral trapping includes the reaction of CO_2 gas with Mg- and Ca-rich minerals forming new more stable carbonate phases.

Mineral carbonation is one of alternative method for carbon dioxide disposal. It was introduced for the first time by Seifritz (1990). This method is assumed to be more efficient way in sequestering CO_2 because the formed carbonates are thermodynamically stable over the long time (Goff and Lackner, 1998). 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 (Wang et al., 2017).

Two options of mineral carbonation technology are currently recognized (e.g. *in situ* and *ex situ*). *In situ* mineral carbonation involves the injection of CO_2 into subsurface reservoirs to enhance the reaction of CO_2 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 (Sanna et al., 2014; Aminu et al., 2017). Production of stable carbonate phases may take place through reaction between CO_2 and alkaline earth as following equations:

$$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}, \Delta H = -179 \text{ kJ mol}^{-1} ......(1)$$

$$MgO_{(s)} + CO_{2(g)} \rightarrow MgCO_{3(s)}, \Delta H = -118 \text{ kJ mol}^{-1} .....(2)$$

Ultramafic rocks are widely distributed in Sulawesi Island. These rocks are the fragments of East Sulawesi Ophiolite (Kadarusman et al., 2004). The objective of this study was to characterize the mineralogy and bulk rock and mineral chemistry of ultramafic rocks from Latowu area and their potential use as material for CO_2 sequestration.

Materials and Methods

Fourteen ultramafic rock samples used in the present study were collected from abandoned nickel laterite mine in the Latowu village of North Kolaka Regency, Southeast Sulawesi (Figure 1). Microscopic analysis was carried out under polished-thin sections using polarizing microscope (Nikon; Eclipse-LV100) either on reflection or refraction mode.

Representative rock samples were crushed by means of jaw crusher followed by manual grinding using agate mortar. Mineralogical composition of the samples was obtained using XRD (Shimadzu, X-7000) with operational condition as follow: 40 kV, 30 mA, scanning range 5 to 70° 2θ; scanning step 0.02° and duration 2°/minute. Bulk rock geochemisty was determined by XRF spectrometer (Rigaku). Mineral chemistry of selected rock samples was analyzed by means of Electron probe microanalyzer (EPMA, JEOL-JXA 8800).
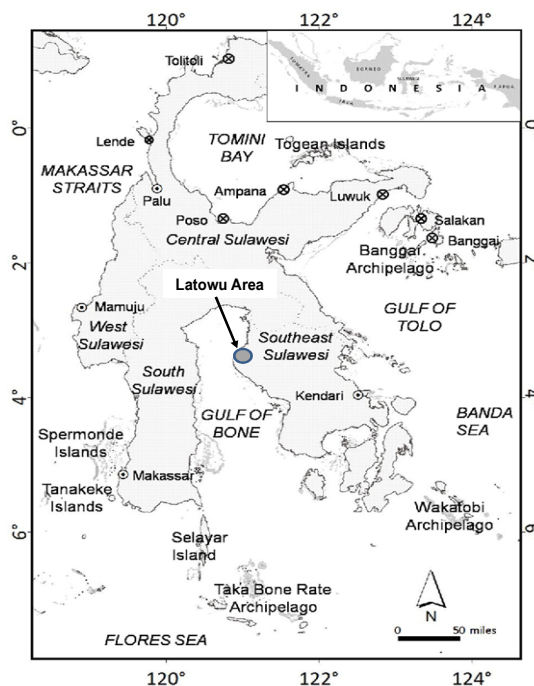

Figure 1. The map showing sample location area

Results and Discussion

Petrographic and mineralogical features

Microscopic observation combined with scanning electron microscope (SEM) examination indicated that almost all samples has been serpentinized with strong to complete degree. Serpentinization is widespread and slightly uniform. In several strongly serpentinized rock samples, pseudo-morphic (mesh) texture after olivine were easily observed. Both ortho- and clino-pyroxene have also been pseudomorphicly replaced by serpentine forming bastite texture (Figure 2). Some analyzed samples, however, show the remnant of olivine and the original shapes of pyroxene crystals were still preserved. Total amounts of serpentine range from 50 to 90 vol%. The presence of olivine relics, pyroxenes and chromite may provide information on the original texture of rocks. Magnetite occurs mainly as filled-fracture veinlets and its occurrence is related to serpentinization.

Secondary serpentine in the form thin veins were commonly observed and they cross cut the pre-existing phases such as serpentine mesh, spinel and locally pyroxene bastites. Few samples show the orthopyroxene grains locally

transformed into talc and tend to develop as outer rims around these crystals. The original mode estimated about 60 to 90 vol% of olivine, 20 to 30 vol% of orthopyroxene, 5 to 10 vol% clinopyroxene, and up to 3 vol% spinel. This indicated that the protolith was dominated by harzburgite and less dunite.
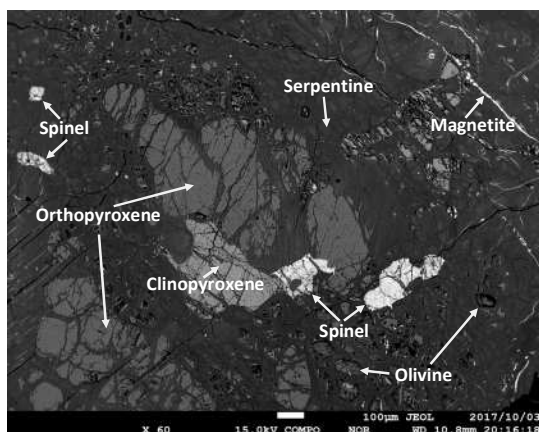

Figure 2. SEM image of an ultramafic rock sample from Latowu

Diffractograms of selected ultramafic rock samples are shown in Figure 3. All samples predominantly compose of lizardite, a serpentine mineral group. It is characterized by the presence of reflection intensity with dspacing including 7.30Å; 3.65Å; 2.51Å and 1.53Å. Chrysotile is another serpentine end-member which has been detected in the analyzed samples. It was indicated by the occurrence of peaks with d_{hkl} of 8.11 Å. Other peaks overlapping with lizardite such as 7.30 Å; 3.65 Å; 2.51 Å also belong to chrysotile. Olivine was identified by the presence of reflections with d value of 4.05Å and 2.78Å. Trace magnetite was also detected on the studied samples. Its occurrence was shown by the signature with d_{dkl} of 2.95Å; 1.70Å and 1.62Å.
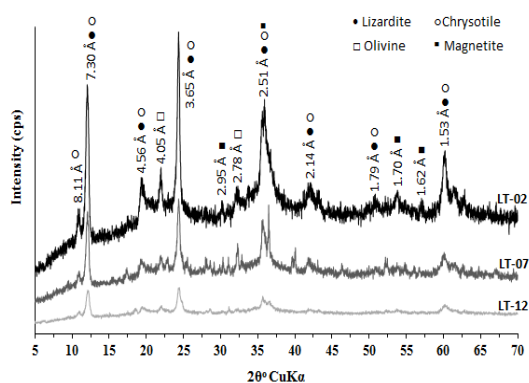

Figure 3. X-ray diffraction patterns of selected ultramafic rock samples from Latowu

Bulk rock chemistry

Table 1 displays major and trace element composition of ultramafic rock samples from Latowu area. It is shown that three elements (e.g. silicon, magnesium and iron) have significant content of the rock. Concentration of SiO_2 ranges between 37.87 and 41.51 wt% with an average of 39.82 wt%; whereas MgO content is between 33.39 wt% and 39.45 wt% with mean of 37.33%. The grade of Fe_2O_3 lies within the range from 6.98 wt% to 10.06 wt% with an average of 8.19 wt%. The average content of LOI is 12.39 indicating that mostly rock has been undergoing strongly serpentinization. Ratio of MgO/SiO_2 ranges between 0.88 and 1.10 with mean value of 0.94.

Chromium and nickel are two most significant trace elements containing in the samples in which Cr has wide range values from 384 ppm to 2605 ppm with the average of 1576 ppm. Likewise, concentration of Ni lies in the range between 1060 ppm and 5906 ppm with an average of 2266 ppm. Other trace elements such as Co and V also have elevated values.

Mineral chemistry

Representative chemical composition of minerals containing in the ultramafic rock from Latowu is given in Table 2. It is indicated that olivine, which predominantly primary mineral occurring in the studied rocks, has relatively low in MgO. However, it seems to be higher in FeO. The ideal MgO and FeO contents of olivine are ~56 wt% and ~2 wt% respectively (Deer et al., 1992). Olivine is an ortho-silicate mineral meaning that it is formed by a number of Si-O tetrahedra linking to Mg-O octahedra (Sufriadin et al., 2011). This mineral, therefore, has no bridging oxygen in its structure. Higher SiO_2 and the concentration of MgO of orthopyroxene reveals that it includes enstatite. On the basis of EPMA data for clinopyroxene as shown in Table 1, it is estimated that such mineral belongs to augite. Both ortho- and clinopyroxene include chain silicate group but orthopyroxene has more simple stucture than clinopyroxene (Deer et al., 1992).

Chemical composition of serpentine is reported in anhydrous basis. If an ideal moisture content of serpentine (~13 wt%) is assumed, then SiO_2, MgO and FeO concentrations of the analyzed serpentine would be 40.63 wt%, 38.30 wt% and 7.64 wt% respectively. Those values are closed to the composition of iron-rich lizardite (Evans, 2008). Serpentine is a sheet silicate group having 1:1 layer. In serpentine structure, tetrahedral sheet is built with silicon as central atom and is bound to four oxygens, whereas

octahedral sheet is framed with one Mg^{2+} cation in the centre and is bound to eight anions (O^{2-} or OH) at the corner (Meunier, 2005). Spinel and magnetite are oxide phases that commonly associated with ultramafic rocks. However, their presence are only in small quantity (<5%).

Table 1. Bulk rock major and trace element compositions of ultramafic rock samples from Latowu area.

Comp. (wt%	LT-02	LT-03	LT-04	LT-05	LT-07	LT-08	LT-09	LT-10	LT-11A	LT-11B	LT-12	LT-13	LTD-31	LTD-33	Av.
SiO_2	41.51	38.29	39.52	39.98	41.17	40.18	39.43	40.46	41.12	40.42	38.73	42.82	35.94	37.87	39.82
Al_2O_3	1.01	0.53	0.83	0.93	1.17	1.22	0.86	1.06	0.79	0.29	0.14	1.01	0.42	1.13	0.81
TiO_2	0.02	0.01	<0.01	0.01	0.02	0.01	0.01	0.01	<0.01	0.01	<0.01	0.02	<0.01	0.02	0.01
MgO	36.48	37.93	38.05	37.98	37.03	37.46	38.16	38.97	36.54	35.74	38.07	33.39	39.45	37.37	37.33
Fe_2O_3	7.95	8.01	8.37	6.98	8.26	8.35	8.46	7.76	8.01	10.06	8.65	8.77	7.62	7.37	8.19
MnO	0.10	0.10	0.11	0.09	0.11	0.11	0.11	0.10	0.09	0.10	0.09	0.11	0.11	0.11	0.10
CaO	0.43	0.39	0.43	0.79	0.99	0.70	0.39	0.77	0.21	0.05	0.03	0.67	0.05	1.67	0.54
K_2O	0.01	0.01	<0.01	0.01	0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.01
Na_2O	0.08	0.03	0.04	0.08	0.05	0.04	0.04	0.04	0.03	0.03	0.03	0.04	0.03	0.07	0.05
P_2O_5	0.01	0.01	0.01	0.01	0.01	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LOI	12.10	13.80	11.20	12.60	10.80	10.90	11.60	10.20	12.40	12.50	13.60	12.10	15.80	13.90	12.39
Total	99.69	99.11	98.56	99.46	99.62	99.01	99.07	99.39	99.20	99.21	99.35	99.35	98.94	99.43	99.52	99.25
MgO/SiO_2	0.88	0.99	0.96	0.95	0.90	0.93	0.97	0.96	0.89	0.88	0.98	0.78	1.10	0.99	0.94
Trace Elements (ppm)															
Ba	2.51	0.32	0.74	0.65	0.32	bdl	bdl	0.16	0.67	3.42	0.42	3.25	0.29	0.27	0.93
Cr	2604.95	2347.47	2208.96	2221.51	1977.10	745.91	1396.30	1631.22	1076.17	595.84	383.69	1460.89	1548.36	1865.50	1575.99
Co	110.21	117.03	109.64	96.94	92.45	52.61	94.76	92.36	93.44	98.31	105.50	96.93	91.89	84.94	95.50
Cu	2.59	8.00	1.72	0.67	10.61	10.84	6.47	6.61	4.83	0.81	1.42	15.46	1.71	4.14	5.42
Pb	0.04	0.20	0.06	0.01	0.38	0.02	0.04	bdl	bdl	0.02	0.01	bdl	bdl	bdl	0.06
Zn	38.50	41.92	48.64	31.54	34.73	22.72	39.35	34.08	31.16	40.26	408.89	83.07	29.80	29.23	65.28
Mo	0.06	0.05	0.08	0.04	0.27	0.05	0.11	0.05	0.04	0.02	0.09	0.04	0.45	0.02	0.10
Ni	2267.37	2504.12	2177.48	2073.73	1888.85	1059.62	1862.91	1883.32	1882.47	2418.48	2186.90	5906.17	1886.37	1731.45	2266.37
Hf	0.21	0.10	0.19	0.10	0.28	0.41	0.21	0.30	0.20	0.08	0.07	0.12	0.27	0.32	0.20
Rb	0.10	0.04	0.05	0.06	0.10	0.02	0.02	0.06	0.15	0.04	0.04	0.12	0.06	0.05	0.07
Sb	0.02	0.01	0.01	0.01	0.01	0.15	0.05	0.03	0.02	0.04	0.07	0.03	0.01	bdl	0.03
Sr	0.92	2.29	0.40	1.31	1.25	0.52	0.50	0.57	0.82	4.71	0.69	3.30	1.17	5.30	1.70
Sc	11.13	6.65	8.88	8.83	9.71	5.55	6.79	7.48	7.39	5.04	3.42	8.94	7.54	8.13	7.54
V	51.25	23.85	35.38	30.19	47.88	24.78	26.53	31.78	25.96	23.00	3.64	40.79	32.77	37.84	31.12
W	0.27	0.22	0.15	0.24	0.32	0.15	0.16	0.20	0.16	0.41	0.03	0.31	0.11	0.24	0.21
Y	0.27	0.22	0.15	0.24	0.32	0.15	0.16	0.20	0.16	0.41	0.03	0.31	0.11	0.24	0.21

Table 2. Representative EPMA data of minerals containing in the selected ultramafic sample from Latowu area.

| Oxide	Minerals					
(wt%)	Ol	OPX	CPX	Srp*	Spl	Mag
SiO_2	40.99	52.43	50.70	46.71	0.28	2.27
TiO_2	0.00	0.00	0.21	0.00	0.00	0.00
Al_2O_3	0.00	3.87	4.04	0.00	49.81	0.00
MgO	48.61	33.77	14.49	44.02	14.56	1.79
CaO	0.00	1.12	26.90	0.00	0.00	0.00
MnO	0.29	0.46	0.24	0.00	0.00	0.00
FeO	9.51	7.38	2.31	8.78	13.03	94.03
Cr_2O_3	0.00	0.95	1.11	0.00	22.03	0.00
NiO	0.61	0.00	0.00	0.49	0.29	0.62
Total	100.01	99.98	100.00	100.00	100.00	98.71

Note: *anhydrous basis, Ol = olivine, OPX = orthopyroxene, CPX = clinopyroxene, Srp = serpentine, Spl = spinel, Mag = magnetite.

Implication to carbon dioxide sequestration

It is commonly recognized that the rocks containing silicate minerals with elevated concentration of magnesium are favorable for carbon dioxide storage. In addition, the physical properties of the rocks such as porosity/permeability, fractures and stress regime may influence carbonation process. Therefore, it should be critically evaluated prior to implement the mineral carbonation technology (Aminu et al., 2017). With respect to mineralogical and geochemical perspective, ultramafic rocks in the Latowu area exhibit good potential as candidate materials for CO_2 disposal. Although almost all olivines have been altered to serpentine, the average magnesia concentration of such rocks is still high (>37 wt%, see Table 1). Moreover, physical properties of the rocks also changes

during serpentinization such as reduction of grain size and density. Those conditions may promote reaction rate due to increase specific surface area of minerals and porosity of the rock being concerned. Carbonation of serpentine with CO_2 can be proceeded through the following reaction (Krevor et al., 2009):

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O ....(3)$$
serpentine   *magnesite silica*
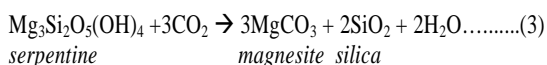
It is shown at the Equation 3 that, in addition to magnesite, reaction between serpentine and carbon dioxide also produces silica. Such material is amorphous and reactive. Therefore it is good potential as raw material in production of silicon carbide (Hirasawa and Horita, 1987).

If *ex situ* mineral carbonation is considered, Styles et al. (2014) found out that extraction rate of Mg from lizardite using 1.4M ammonium bisulfate has reached up to 80% after 1 hour. Similarly, Mg extraction from olivine could be gained up to 55%. In contrast, recovery of Mg from antigorite has only achieved less than 40% after 1 hour reaction. While pyroxene has slow dissolution with only 25% Mg exteraction has been achieved.

Dissolution rates of metals from silicate minerals in acid solution are also affected by crystal structure, crystallinity and metal content. Leaching experiment using sulfuric acid conducted by Liu et al. (2010) concluded that fast dissolution rate takes place preferentially for lizardite having lower crystal order and low in aluminum, but higher in iron. The higher iron content of serpentine in the Latowu ultramafic rocks (see Table 2) may confirm rapid dissolution of this mineral in acid solution. Chemically bound water in serpentine structure may also has an influence in increase of chemical reactivity (Lackner et al., 1995). Dehydroxilation of serpentine may take place at the temperature above $550^{\circ}C$, leading to produce amorphous material (Dlugogorski and Balucan, 2014).

Despite the application of mineral carbonation is techically viable, however, in terms of economic feasibility, those methods are still expensive. It is therefore required to consider re-using the products (e.g construction, additive, high tech. materials) in order to promote public acceptance in the application of mineral carbonation technology (Olajire, 2013).

Conclusion

This study presents mineralogical and geochemical signature of the Latowu ultramafic rocks in relation to their suitability as candidate materials for carbon dioxide storage. Results show

that mostly primary minerals have been replaced by serpentine mainly lizardite. This alteration has not only changed mineralogy but also physical properties of the rocks. Bulk chemical compositions reveal relatively high magnesium and iron. Similarly, at the mineral scale, serpentine is fine grained, higher in Mg and Fe and hydrous. This is beneficial in mineral carbonation process due to the increase specific surface area and porosity, leading to accelerate chemical reaction. However, some drawbacks are associated with the application of mineral carbonation both *in situ* and *ex situ* options. The limitation of *in situ* method is considerably slow reaction rate so that the process efficiency is difficult to evaluate; whereas the operational cost of *ex situ* method is still high because it requires comminution and transportation of the materials along with solvent and catalyst.

Acknowledgements

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