Mobility of rare earth element in hydrothermal process and weathering product: a review

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Abstract. The Rare Earth Element (REE), consists of La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Lu, Ho, Er, Tm, Yb, are important elements to be used as raw materials of advanced technology such as semiconductors, magnets, and lasers. The research of REE in Indonesia has not been done. Several researches were conducted on granitic rocks and weathering product such as Bangka, Sibolga, West Kalimantan, West Sulawesi and Papua. REE can be formed by hydrothermal processes such as Bayan Obo, South China. The REE study on active hydrothermal system (geothermal) in this case also has the potential to produce mineral deposits. The purpose of this review paper is to know the mobility of REE on hydrothermal process and weathering products. Mobility of REE in the hydrothermal process can change the distribution patterns and REE content such as Ce, Eu, La, Lu, Nd, Sm, and Y. Another process besides the hydrothermal is weathering process. REE mobility is influenced by weathering products, where the REE will experience residual and secondary enrichment processes in heavier minerals.

1. Introduction
In recent years, a relationship between demand and supply of Rare Earth Element (REE) resources has been becoming tight in the world market [1]. The REE is the intended element in the lithophyl group which has a tendency to be dispersed since its formation as a trace in minerals [2]. The REE group is composed of 15 elements that range in atomic number from 57 (lanthanum) to 71 (lutetium) on the periodic table of elements, and are officially referred to as the “lanthanoids,” although they are commonly referred to as the “lanthanides. The REEs are divided into two groups on the basis of atomic weight: the light REE are lanthanum through gadolinium (atomic numbers 57 through 64), and the heavy REE comprise terbium through lutetium (atomic numbers 65 through 71). The REE consists of La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Lu, Ho, Er, Tm, Yb, which are important elements to be used as raw materials of advanced technology such as semiconductors, magnets, and lasers [2]. Besides that, the industry’s need for REE is critical in high-tech applications [3]. The REE encountered in the earth’s crust was higher than that of the element Au, Mo, As dan Be. In Indonesia REE are founding minerals in some major commodities that has the opportunity to be cultivated as byproducts that can provide added value from all potential minerals.

REE of non-volcanic rock research is very interesting because Indonesia consists of islands and some of them have composite alkaline acid rocks which contain monasit, xenotim, zircon, ilmenit, and kaskiterit minerals as the REE source. The REE is found in alkaline acid rocks in the environment of continental geology [4]. The REE research in Indonesia has not been done. Several researches were conducted on granitic rocks and weathering product such as in Bangka [5], Sibolga [6], West Kalimantan, West Sulawesi and Papua [7]. The REE can be formed by hydrothermal processes such as
Bayan Obo, South China [8]. High REE is found more frequently in granitic rock. REE in non-volcanic areas is found on granitic rocks with Sn, W, Be, Nb, Ta, and Th compositions founding in Granite S type or ilmenite series. In Indonesia the distribution of REE is often found in Sumatra, Bangka Belitung, Kalimantan, Sulawesi and Papua. REE is related to hydrothermal process especially geothermal fluids, where it is a potential source of mineral such as REE [9], and important material for future energy source and economical value [10].

REE can also be used to determine the source of fluid magma and fluid system in the rocks [11]. The composition of hydrothermal fluid is one of the important parameters that affect REE transportation activity and type hydrothermal alteration. Besides that, source rocks type is greatly affect the abundance of the REE element in the geothermal area [9]. Mobility of REE in hydrothermal fluids involves complex formation of carbonate, fluoride, and sulfate. Several mineral studies in the geothermal environment obtained an indication of REE in the form of elements La, Ce, Y and Nd. The element reaches the maximum until 2.0 ppm. Study of the Larderello-Travale geothermal system revealed complete REE patterns including Y henceforth referred to as REY in the range 0.01–5 pmol/l, with vapor–liquid partitioning factors of about 0.2 [11]. This paper reviews the state of the art mobility of rare earth element in hydrothermal process and weathering products “Non-volcanic geothermal areas in Indonesia”.

2. Mobility of rare earth element
Several studies have suggested that REE are immobile during metamorphism or hydrothermal alteration [12-16], also the extremely low REE concentrations in hydrothermal fluids have been suggested as evidence that the REE budget of host rocks is unaffected by hydrothermal alteration. The REE concentrations in hydrothermal fluids have been shown to range from below detection limits to chondritic values [17]. REE mobility is significantly influenced by hydrothermal processes. This has led to the REE content of geothermal fluids and precipitated alteration minerals may be used as tracers for geothermal fluids and processes [17,18].

Geothermal area is formed at volcanic arc environment role heat source. Many alterations occur in side rocks, where hydrothermal fluids can alter the distribution patterns and REE elements such as Ce, Eu, La, Lu, Nd, Sm, and Y. The alteration process is related to the level of mobility of the REE element in the hydrothermal process. The characteristics of hydrothermal fluid in the alteration process have high variables. The characteristics of hydrothermal fluid depend on the origin of the magma. REE mineralization occur in some deposit types; e.g. carbonatite rock formation, granitic rocks, manganese deposit, hydrothermal iron-ore deposit, placer deposit, lateritic soil, ion adsorption weathering crust and uranium deposit [19].

REE deposits can broadly be divided into two categories; primary and secondary deposits [20]. Primary deposits are results of magmatic or hydrothermal processes whilst secondary deposits are concentrated by weathering and lateritization processes [21]. Primary deposits are associated with igneous rocks which are relatively rich in Light-REE (LREE). Primary minerals containing REE in primary deposits may include bastnasite, monazite, xenotime, eudayte, allanite, zircon, apatite, and a variety of more uncommon minerals. The mineral may contain Cerium elements that also contain metal oxides such as lanthanum and neodymium. Cerium is an REE with oxide compounds of lanthanum metal, samarium, praseodymium, neodymium, promethgium and europium. REE in the geothermal region is strongly influenced by the hydrothermal mobility formed by sulfur acid fluids that may be found at the top of a volcano or around the caldera rings. This is a place of groundwater mixing with magmatic gas rising to the surface. Another process besides the hydrothermal process is weathering process.

REE resource can be found in various types of deposit. One of them is the laterite REE deposits which then develop into ion-adsorption type deposits, such as in Longnan Province, Southern China. Weathering product greatly affects the mobility of the elements, where the elements with the lowest to static mobility such as those belonging to the REE experience both residual and secondary enrichment. Basically, the enrichment of the REE element is not a common thing, although rarely found
economically. The enrichment of REE in the weathered granitic rocks can be found in two types, namely: placer deposit and ion-adsorption type deposit. The typical of the granitic rocks which enriched in REE is predominantly I-type granitic rocks.

REE are adsorbed on clay (e.g. kaolinite, halloysite) and can be extracted by ion-exchangeable electrolyte solution. The ion-adsorption deposits are formed by chemical weathering of rocks and subsequent chemical adsorption of REE at kaolinite and halloysite [22]. The REE content in the chemical weathering product of rocks has adsorption ions generally varying from 300 to 2000 p.p.m. depending on the parent rock [2,19,23]. The weathered can be divided into the A, B and C horizons. The A horizon consists of soil layer with dark brown to reddish dark brown soil. This top layer is enriched in organic matter and clay mineral, whereas primary rock-forming minerals are not recognized. The B horizon is brown to reddish brown and consists of weathering product. The B horizon is enriched in REE relative to the parent rocks whereas the A and C horizons are generally depleted or less enriched in REE.

The weathering process starts from the infiltration of acidic rainwater and then enters the rock fracture zone and will dissolve the soluble minerals in the bedrock. High density minerals such as hematite, magnetite, monazite, xenotime will be left on the surface and experience residual enrichment. The other minerals with low densities will be transported and experience residual enrichment process. Enrichment or depletion of REE occurs because these elements are mobile and they are fractionated during weathering [24]. The relative enrichment of REE in the weathering products in relation to bedrock is pronounced in horizon B [25].

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