INVESTIGATION OF POTENTIAL WEATHERED REE-BEARING GRANITOID CRUST FROM DINDING DISTRICT OF WESTERN TIN BELT, PENINSULAR MALAYSIA

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by

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In God's Most Beneficent Name

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LIST OF SYMBOLS

°C	Degree Celsius or centigrade
Å	Angstrom
µm	Micrometre
LU	Lumut site
TM	Telok Murok site
cm	Centimetre
mm	Millimetre
Km	Kilometre
gr	Gram
mL	Millilitre
M	Molar
V	Volume
Ma	Mega Annum
Ga	Gallium

LIST OF ABBREVIATIONS

REE	Rare Earth Element
LREE	Light Rare Earth Element
HREE	Heavy Rare Earth Element
REO	Rare Earth Oxide
IAD	Ion-adsorption Deposit
Qtz	Quartz
Apt	Apatite
Mon	Monazite
Alla	Allanite
Zr	Zircon
Bt	Biotite group minerals
Chl	Chlorite
Plg	Plagioclase
kfs	K-feldspar
UTM	Universal Transverse Mercator coordinate system
IOA	Iron Oxide–Apatite deposits
IUPAC	International Union of Pure and Applied Chemistry
SIAM	Sedimentary-Igneous-Anorogenic-Mantle
IUGS	International Union of Geological Science
ppm	Part Per Million
wt. %	weight percentage
f	Fugacity
PC	Partitioning Coefficient
ASI	Aluminium Saturation Index
CIA	Chemical Index of Alteration
MALI	Modified Alkali Lime Index

XRF	X-ray Fluorescence Spectroscopy
XRD	X-ray diffraction
OM	Optical Microscopy
SEM-EDX	Scanning electron microscope - energy-dispersive X-ray
FTIR	Fourier Transform Infrared
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
CEC	Cation Exchange Capacity
MORB	Mid-Oceanic Ridge Basalt
OIB	Oceanic Island Basalts
IMA	International Mineralogical Association
GOE	Great Oxidation Event
PZC	Point of Zero Charge
GPa	Giga Pascal
EMPA	Electron Microprobe Analysis
LA-ICP-MS	Laser Ablation Inductively Coupled Plasma Mass Spectrometry
ASTM	American Society for Testing and Materials
CI	Carbonaceous Ivuna chondrite
LOI	Loss on Ignition
kgf	Kilogram Force
IDL	Instrumental Detection Limit
EG	Ethylene-Glycol
HDD	Hard Disc Drive
Dep.	Department
CNMMN	Commission on New Minerals and Mineral Names
SI	International System of units
SERC	Science and Engineering Research Centre
SMMRE	School of Materials and Mineral Resources Engineering
IPS	Institute of Postgraduate Studies
USM	Universiti Sains Malaysia

KAJIAN POTENSI GRANIT TERLULUHAWA BAGI UNSUR NADIR BUMI (REE) DARI DAERAH DINDING, JALUR TIMAH BARAT SEMENANJUNG MALAYSIA

ABSTRAK

Penyelidikan strategik ini menafsirkan penerokaan hijau dan mampan unsur nadir bumi (REE) endapan tanah jenis penjerapan ion dengan isu radioaktif minimum atau bebas di beberapa kawasan barat Semenanjung Malaysia. Kajian pencirian intensif dijalankan terhadap dua set sampel dari daerah Dinding yang terletak di bahagian barat jalur granit timah Malaysia. Memahami ciri-ciri dan perlakuan geokimia REE di kalangan granitoid terluluhawa serta keboleh proses larutlesap adalah objektif utama kajian ini. Kajian ini dijalankan berdasarkan maklumat lapangan dan kajian teknik mikroskopik, XRD, Spectroscopy FTIR, SEM-EDX, XRF, ICP-MS, penentuan CEC dan keboleh larutlesap REE yang dihoskan oleh tanah. Kajian petrografi dan analisis geokimia menunjukkan granitoid di tapak Lumut (LU) dan Telok Murok (TM) adalah siri ilmenit, terutamanya peraluminous, jenis-S yang diklasifikasikan sebagai syeno-granit dan monzo-granit, masing-masing dengan k-feldspar, kuarza, plagioklas dan mika sebagai mineral utama. Apatit, monazit, zirkon, allanit, titanit dan ilmenit adalah mineral aksesori utama di tapak LU manakala tapak TM mengandungi terutamanya zirkon, apatit dan allanit. Analisis XRD menunjukkan kehadiran kumpulan tanah liat kaolin dan smektite, manakala phlogopite merupakan mika lazim dalam granit induk. Di kedua-dua lokasi, pengurangan kandungan REE+Y (REY) di horizon A agak ketara, manakala REY meningkat di horizon B dan / atau C. Kandungan maksimum REY boleh setinggi 3500 ppm di horizon B2 dan / atau C dari analisis ICP-MS. Jumlah kandungan

REE (TRE) bagi lempung terluluhawa adalah agak tinggi secara relative berbanding dengan batuan induk (3 hingga 7 kali), pada kedua-dua lokasi di horizon B dan C. Gambarajah normilasi konderit menunjukkan kecenderungan Ce menurun dari anomali positif kepada negatif dengan pengkayaan LREE di kedua-dua lokasi. Walaubagaimanapun, jisim keseimbangan komponen mineral REE di antara setiap horizon di kedua-dua tapak adalah berbeza. Dalam eksperimen pelarutlesapan kelompok, kecepakan pengekstrakan TRE adalah sebanyak ~ 70% - 90% bagi kedua-dua tapak manakala kadar pengekstrakan yang lebih rendah sebanyak 50-80% diperolehi bagi HREEs.

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ABSTRACT

This research interpreted a green and sustainable exploration strategy of ion-adsorption type REE clay potential deposits with minimum or free radioactive issues in some prone districts of western Peninsula Malaysia. An intensive characterization study was conducted on two sets of samples from Dinding district located within the western part of Malaysian tin granite belt. Understanding REEs characterization and geochemical behaviour among weathered crusts of granitoids as well as their leachability were the main objectives of this study. The study was conducted based on the field and microscopic investigations, XRD, FTIR Spectroscopy, SEM-EDX, XRF, ICP-MS, CEC determination and batch leaching of clay hosted REEs. Petrographical study and geochemical analysis showed granitoids in Lumut (LU) and Telok Murok (TM) sites were ilmenite-series, mainly peraluminous, S-type which were classified into syeno-granite and monzo-granite, respectively with k-feldspar, quartz, plagioclase and mica group as major minerals. Apatite, monazite, zircon, allanite, titanite and ilmenite were accessory minerals in LU site whilst, TM site was indicated by zircon, apatite and allanite. XRD analysis showed the presence of kaolin and smectite rich clay groups, whilst phlogopite was common mica in parent granites. In both sites, depletion of REE+Y (REY) content in horizon A was considerably apparent, whilst REY enriched in horizon B and/or C. The maximum content of REY could be as high as 3500 ppm in horizon B2 and /or C analyzed by ICP-MS. Total REE content (TRE) of the weathered crust is relatively elevated compared to the parent rocks (3 to 7 times), in horizon B and C of both sites. The chondrite normalized diagrams showed a downward tendency of positive to negative Ce anomaly with LREE enrichment in both sites. However, the mass balance of REE mineral components between each horizon in both sites are different. In batch leaching experiments, TRE extraction levels of ~70% ~ 90% for both sites were achieved with relatively lower extraction of 50-80% for HREEs.

CHAPTER 1

INTRODUCTION

1.1 Rare Earth Elements (REE)s

Rare earth elements (REEs) stand for the set of seventeen elements including fifteen lanthanides: lanthanium (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu) along with yttrium (Y) and scandium (Sc) (Meija et al., 2016; Xiao et al., 2016). They are normally grouped depending on the atomic number, into "light" rare earth elements (LREE) - La, Ce, Pr, Nd, and into "middle and heavy" (HREE) - Sm, Eu,Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu. Notwithstanding their name, REEs - except for the radioactive Pr – are relatively abundant in Earth's crust, with cerium being the 25^{th} most abundant element at 68 parts per million (ppm), more abundant than copper. Even, the two least abundant REE (Tm, Lu) are nearly 200 times more common than gold. Conversely, because of their very similar geochemical properties, REEs are typically very difficult to be separated from each other (Haxel et al., 2002).

Geologically, excluding continental rifts which are the host of carbonatite and kimberlites (Hoshino et al., 2016), it was proven that REEs enriched in REE-bearing minerals of igneous rocks such as apatite, allanite, monazite, titanite, xenotime and etc. in the lower mantle during magmatic differentiation (Castor and Hedrick, 2006). Generally, REEs deposits divide up according to their mineralogy and geneses into two types of primary deposits associated with igneous and hydrothermal activities and secondary deposits assembled by sedimentary processes and weathering (Lusty and

Walters, 2010). Two significant types of secondary deposits are the placer and ion-adsorption clays deposits. The latter which called “regolith-hosted REEs” is originated from high REE content plutonic or volcanic rocks weathering process resulted in accumulation of REEs in igneous weathering profiles (Hoshino et al., 2016). Ion-adsorption clay deposits consider being the host of more than 80% of middle and heavy REEs (Hu et al., 2017).

However, Koppen-Geiger climate classification suggested that temperate and tropical sites are potential zones for weathered granite or ion-adsorption clay type REE resources, thus promoting of intensive chemical weathering and breakdown of REE-bearing minerals by such climate conditions (Peel et al., 2006; Sanematsu and Watanabe, 2016). Malaysia with the wide distribution of S/I-type granite and annual rainfall of 2500 ml, has a high potential in the occurrence of this type of deposits.

Thailand-Malaysia-Western Indonesia has been known as the Southeast Asian tin-granite belt, a major metallogenic province of Sn deposits associated with Ilmenite, S and/or I-type series of granitic rocks (Ishihara, 1981, 1998; Chappell and White, 2001; Imai et al., 2013;). Three granitic belts to be exact “Eastern belt” with a high portion of I-type granites, “Central belt” with a high portion of S-type granites and “Western belt” with a mixture of I and S-type granites were indicated in that region (Figure 1.1). A line parallel to Bentong-Raub closure considered to be the separator of the Western and Eastern Malaysian granite (Metcalfe, 2013) which is presented in Figure 1.1.

Geochemically, vertical fluctuation of REE grade among profile is utilized to study of REE behaviour in granitic weathering profiles and yield an evaluation of geochemical mechanisms for REE fractionation and mobilization.

This research reports the first intensive study on characteristics, whole-rock geochemistry and mineral chemistry of REEs associated with weathered crust of western Malaysian granite belt (Dinding granite) and their parent rocks.

1.2 Research background

Malaysia already has a long experience in the upstream REE industry, used to be a producer of REE minerals for several decades from alluvial tin granite mining by-product in Kinta Valley (5% of world production in 1993). Malaysian xenotime used to be the main source of yttrium before 1988 (The academy of Science of Malaysia and The National Professors' Council, 2011). Xenotime, monazite, zircon, ilmenite and struverite were produced as the by-product of tin-mining in Malaysia for several decades. Ti minerals were subjected to further processing to produce TiO_2, meanwhile the efforts to REE extraction from monazite and other heavy minerals was hampered by strong presence of Th/U in the minerals (Kamar Shah Ariffin, 2011).

The country also has the experience of being involved in midstream chemical processing of REE minerals to produce REE compounds.

1.2.1 Malaysian REE Resources potential in weathered granitic rocks

South East Asian weathered granitic crusts located in the countries such as Vietnam, Thailand, Laos, Indonesia and Malaysia were subjected to investigate mostly after 2009 under ASEAN Universities Network (AUN) program leaded by Kyushu University, Japan. Previously, no intensive exploration project has been reported on Malaysian "weathered granitic crust associated with REE" potential.