

## Original Article

# Geochemical Behavior of Rare Earth Elements in Weathered Granitic Rocks in Northern Palawan, Philippines

Jenielyn T. PADRONES,<sup>1\*</sup> Akira IMAI<sup>2</sup> and Ryohei TAKAHASHI<sup>2</sup>

<sup>1</sup>Graduate School of Engineering and Resource Sciences, and <sup>2</sup>Graduate School of International Resource Sciences, Akita University, Tegatagakuen-machi, Akita, Japan

## Abstract

Weathered crust of granitic rocks of two geochemically similar plutons that differ in age of magmatism were investigated in the Philippines. These are the Cretaceous Daroctan Granite and the Middle Miocene Kapoas Granitoid located in Palawan Island, a part of the Palawan Continental Block derived from the continental margin of southeastern Eurasia. Both plutons are composed of biotite granodiorite and biotite granite and are geochemically characterized as ilmenite series, high-K calc-alkaline, intermediate I- and S-types, and peraluminous.

Light rare earth element (LREE) content of the weathered granitic crusts in the Kapoas Granitoid is higher than that in the Daroctan Granite, and LREE are enriched in the Daroctan Granite compared to the parent granitic rocks. In both plutons, the residual REE-bearing minerals are mostly monazite. Allanite is only present in the Kapoas Granitoid while the Daroctan Granite contains xenotime. The Kapoas Granitoid pluton shows potential for placer-type LREE deposit as observed in the elevated LREE content of the stream and beach sediments containing La, Ce, Nd and Sm up to >10,000 ppm. Sequential leaching extraction of REE using eight reagents which selectively dissolved REE with different mode of occurrence (i.e. water soluble, ion-exchangeable salts, Pb-displaceable, acid soluble, Mn-oxide occluded, organically-bound, amorphous Fe-oxide occluded, and crystalline Fe-oxide occluded forms), show that the Daroctan Granite has a potential for ion-adsorption type REE resource with proportion of extracted REE ranging from 53 to 74 % among  $\Sigma$ REE. Formation of secondary REE-bearing minerals, such as cerianite formed on the surface of clay minerals, results in enrichment of REE.

**Keywords:** Daroctan Granite, ion adsorption type, Kapoas Granitoid, monazite, Palawan (Continental Block), monazite, Philippines.

## 1. Introduction

Current global distribution of producing countries of rare earth elements (REE) is limited to China, Russia, United States, Brazil, India, Australia, Canada, and Greenland. The historical data of REE production shows that China has been leading the market in the past three decades (Wübbeke, 2013). The increase in the price of REEs has paved the way to various

exploration efforts worldwide to look for deposits outside China (Hatch, 2012). Areas that have ongoing exploration works are in Australia, Brazil, Canada, China, Finland, Greenland, India, Kyrgyzstan, Madagascar, Malawi, Mozambique, South Africa, Sweden, Tanzania, Turkey, and Vietnam (Gambogi, 2015). Among the deposits in China, the Bayan Obo deposit is the primary source of REE, while a relatively high percentage comes from the ion-adsorption type

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Corresponding author: J.T. Padrones, Institute of Renewable Natural Resources, College of Forestry and Natural Resources, University of the Philippines, Los Baños, Laguna 4031, Philippines. Email: jenpadrones@gmail.com

derived from weathered crusts of granitic rocks in southern China. Some recent works on REE deposits are related to the ion-adsorption type. In Southeast Asia, areas with granitic plutons have been revisited for possible enrichment of ion-adsorption type REE deposits (Sanematsu *et al.*, 2009, 2013; Imai *et al.*, 2012).

In the Philippines, previous reports relating to REE mineralization were mostly on the occurrence of REE-bearing minerals such as allanite and monazite in northern Palawan. The area was listed in the United States Geological Survey (USGS) as one of the areas with occurrence of placer-type REE deposits. The Philippine Nuclear Research Institute delineated six areas for La, Ce, Pr, Nd, and Y anomalies in Erawan, Kapoas, Roxas, Babuyan-Langogan, Tanatanaon-Taradungan, and Itangil-Tanatanaon (Reyes *et al.*, 1992). The British Geological Survey, on the other hand, carried out offshore geophysical investigation for heavy mineral exploration using sea bed gamma spectrometry (Ringis *et al.*, 1993), and reported high Th and U radiometric anomalies in Imuruan Bay, near Ombo Beach. However, there has been no study on the mechanism of enrichment of REE in those areas. The enrichment of REE is correlated with the granitic rocks in the study area, which is the Middle Miocene Kapoas Granitoid. The recognition of the Cretaceous Daroctan Granite (Metal Mining Agency of Japan and Japan International Cooperation Agency [MMAJ-JICA], 1988) has opened up new targets for exploration. This study, which was carried out on both plutons, aims to elucidate how the REE were enriched in the weathered crusts. This study also seeks to understand the geochemical behavior of REE and other elements in the weathered crusts.

## 2. Geological background

### 2.1 Tectonic setting

The Palawan Continental Block (PCB, Concepcion *et al.*, 2011; Canto *et al.*, 2012; Palawan–Mindoro Continental Block, Aurelio *et al.*, 2013) is a fragment of the Sundaland–Eurasian Plate, which was translated into its present location due to the rifting of the South China Sea basin during the Late Eocene (Hsu *et al.*, 2004). It collided with Sabah and Cagayan arc in the southeast during the Early Miocene (Hall, 2013) and eventually collided with the Philippine Mobile Belt (PMB) in central Luzon during the Middle Miocene (Walia *et al.*, 2012). Presently, the Philippine archipelago is divided into two major blocks: the

PCB, which is part of the extended continental margin (Franke *et al.*, 2011; Canto *et al.*, 2012; Concepcion *et al.*, 2011; Aurelio *et al.*, 2013; Hall, 2013); and the PMB, which has arc affinity (Yumul *et al.*, 2009; Aurelio *et al.*, 2013).

The study area, Palawan Island, is located in the western part of central Luzon (Fig. 1). It is part of the PCB and composed of allochthonous blocks, some of which are the oldest units in the Philippine archipelago (Yumul *et al.*, 2009; Aurelio *et al.*, 2013). The sliver of the PCB in Palawan Island is composed of Late Cretaceous metasedimentary rocks in the northern and central part (Suzuki *et al.*, 2000; Yumul *et al.*, 2009; Walia *et al.*, 2012; Suggate *et al.*, 2014), and of an oceanic crust overlain by syn-rift sediments in the southern part (Aurelio *et al.*, 2014). Magmatic activities occurred during Middle Eocene (Suggate *et al.*, 2014), Middle Miocene (Encarnación & Mukasa, 1997; Suggate *et al.*, 2014) and Pleistocene (Aurelio *et al.*, 2013).

### 2.2 Granitoids in northern Palawan

The granitic intrusive rocks being investigated in the study are the Cretaceous Daroctan Granite in El Nido (MMAJ-JICA, 1988) and the Middle Miocene Kapoas Granitoid in San Vicente (Encarnación & Mukasa, 1997; Suggate *et al.*, 2014) (Fig. 1).

The Daroctan Granite is a pluton in the northernmost part of Palawan Island. It was assigned to Cretaceous age by MMAJ-JICA (1988). However, the Daroctan Granite has not been recognized in most of the geological works on Palawan Island. It was recognized as a part of the Kapoas Granitoid (also known as Kapoas Granite (Peña, 2008), Mesozoic Melange (Encarnación & Mukasa, 1997; Suggate *et al.*, 2014) or the Jurassic olistrostrom (Suzuki *et al.*, 2000). The Daroctan Granite intruded the Mesozoic melange in the northern part of the PCB. The assigned age correlates with the late episode of the Yanshanian magmatism in eastern China (Li, 2000) and is probably cogenetic with the Mesozoic granites surrounding South China Sea (Yan *et al.*, 2014) and Late Yanshanian granites in eastern China (Zhou *et al.*, 2006). The Daroctan Granite is composed of two intrusive bodies mapped in Barotuan and Tenegueban in El Nido. These units intruded the Bacuit Formation composed of interbedded fine to coarse-grained sandstones, pebbly mudstones, and siliceous sediment. These sedimentary rocks are intensely folded and are highly jointed and faulted.

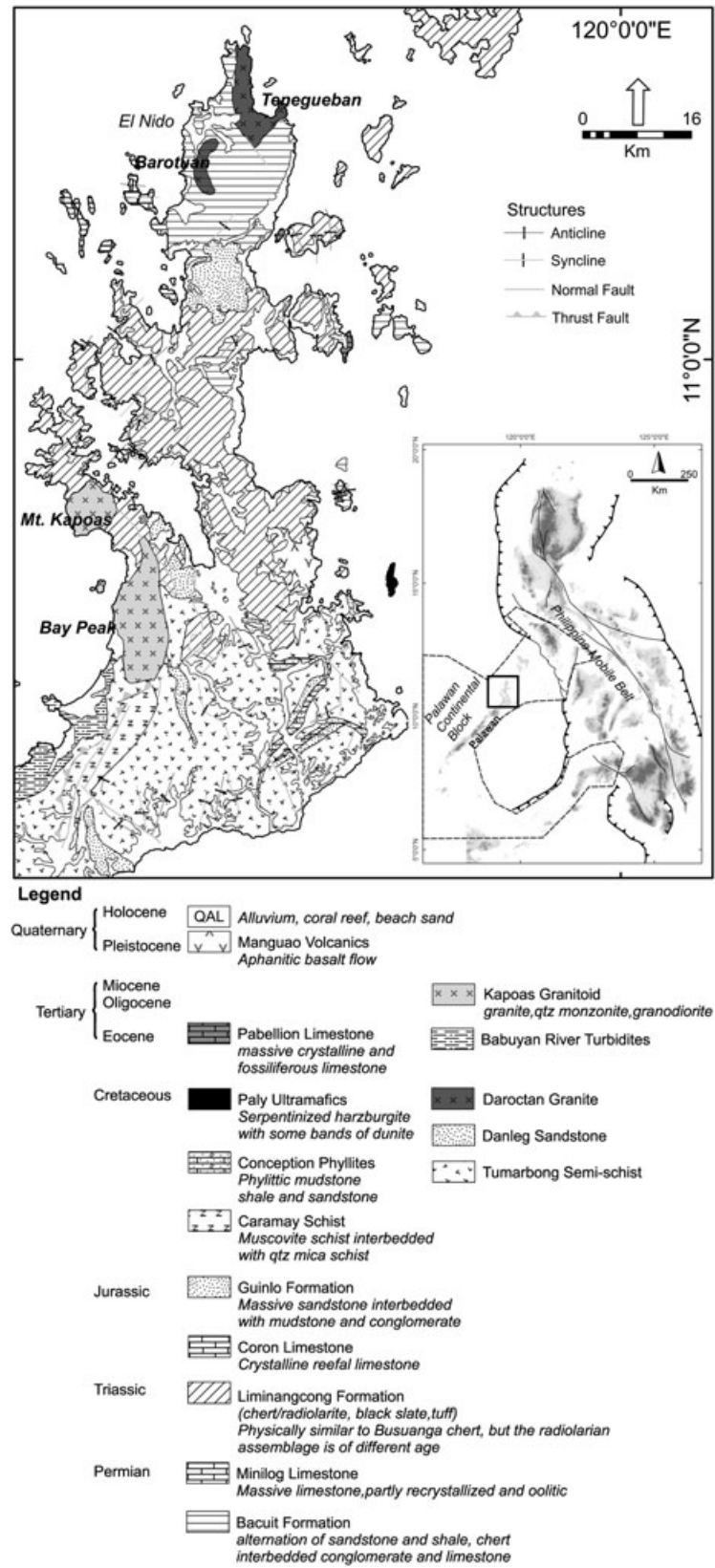


**Fig. 1** Geologic map of the northern Palawan Island showing the plutons being investigated in this study (modified from MMAJ-JICA, 1988). Inset shows the tectonic map of the Philippines showing the different subduction zone surrounding the Philippine island arc, the major structures, and the two major tectonic blocks: the Palawan Continental Block and the Philippine Mobile Belt.

The Kapoas Granitoid, also known as Tiniguiban Granodiorite (Ringis *et al.*, 1993), Capoas Granite (Encarnación & Mukasa, 1997); Capoas and Bay Peak Granite (Suggate *et al.*, 2014), is composed of intrusive bodies, namely; Mt. Kapoas pluton and Bay Peak pluton. The Kapoas Granitoid is the well-studied granitic intrusion in northern Palawan in terms of geochronology, with ages ranging from 15 to 13.4 Ma (U–Pb zircon and monazite dating, Encarnación & Mukasa, 1997),  $13.8 \pm 0.2$  Ma for the Bay Peak pluton and  $13.5 \pm 0.2$  Ma for the Mt. Kapoas pluton (U–Pb zircon dating, Suggate *et al.*, 2014). Based on Suggate *et al.* (2014), the Bay Peak pluton may have intruded 3 my earlier than the Mt. Kapoas pluton. The timing of intrusion relative to the possible location of the rifted PCB fragment suggests that it was formed in an “anorogenic” within plate setting and possibly triggered by basaltic underplating or intraplate magmatism (Encarnación & Mukasa, 1997). The Bay Peak pluton intruded the Late Cretaceous Tumarbong Semi-schists unit (also known as Concepcion Pebbly Phyllite, Suzuki *et al.*, 2001; Concepcion Phyllite, Peña, 2008). The Mt. Kapoas pluton, on the other hand, intruded the chert of the Liminangcong Formation (Encarnación & Mukasa, 1997).

The Kapoas Granitoid is classified into metaluminous, high-K calc-alkaline, and I-type granite formed in the syn-collisional and volcanic arc granite setting (Encarnación & Mukasa, 1997). These geochemical signatures were taken from the source rock of the Kapoas Granitoid melt given that the present-day tectonic setting of the unit is far from any subduction or collision zones (Encarnación & Mukasa, 1997).

### 3. Materials and methods

Clay minerals in the weathered crust of granitic rocks were identified using a Rigaku Multiflex X-ray diffractometer (XRD) and petrographic analysis using a Nikon LV100N polarizing microscope installed at the Department of Earth Resource Science, Akita University. The measurement conditions of XRD are at 30 kV and 16 mA, with scan speed at  $2^\circ/\text{min}$  for the bulk analysis and  $1^\circ/\text{min}$  for the hydraulically-elutriated clay minerals, from  $2$  to  $60^\circ$  and from  $2$  to  $40^\circ$ , respectively. Step width for both analyses is at  $0.010^\circ$ . The hydraulically-elutriated samples were treated with HCl to confirm the peaks of chlorite and kaolinite (Moore & Reynolds, 1997). The chemical composition of minerals was analysed using a JEOL JSM-6610 LV

scanning electron microscope with energy dispersive spectroscope (SEM-EDS). The measurement conditions are at 15 kV acceleration voltage, 2.2 nA probe current and 10 mm working distance.

Field and laboratory measurement of magnetic susceptibility of the parent granite was carried out using a KT5 magnetic susceptibility meter. Whole-rock major element composition of the parent granite and weathered crust samples were analyzed using a Rigaku ZSX Primus II X-ray fluorescence spectrometer (XRF) installed at the Venture Business Laboratory, Akita University. Powdered parent granitic rocks and weathered granitic rock samples were heated at  $900^\circ$  in an oven to measure the loss on ignition (LOI) value, then melted to prepare fused glass bead at 1:5 sample–flux ratio containing 0.80 g of sample, 3 g of di-lithium tetraborate ( $\text{Li}_2\text{B}_4\text{O}_7$ ) and 1 g of lithium metaborate ( $\text{LiBO}_2$ ). Total Fe content is expressed as  $\text{Fe}_2\text{O}_3$ . Whole-rock trace element concentration of parent granitic rock and weathered granitic rock samples were analyzed using inductively coupled plasma–mass spectrometer (ICP–MS) at ALS in Vancouver, Canada. Sequential extraction was carried out on ten representative weathered crust samples from the Kapoas and Daroctan granitoids. The method was adopted from Imai *et al.* (2012), which was modified from the method proposed by Miller *et al.* (1986). The leaching method used eight reagents which selectively extracted REE in different chemical forms in the following sequence: water soluble, exchangeable salts, Pb-displaceable, acid soluble, Mn-oxide occluded, organically-bound, amorphous Fe-oxide occluded, and crystalline Fe-oxide occluded. The REE contents of solution leached from samples per reagent were analyzed using an Agilent Technologies 7500 Series ICP–MS installed at the Department of Earth Resource Science, Akita University. The elements analyzed were limited to REE, Y, Th, and U.

### 4. Results

#### 4.1 Description of the weathered crusts of granitic rocks

Weathered crust of granitic rocks typically consists of different layers which differ in physical and geochemical characteristics (Wu *et al.*, 1990; Sanematsu *et al.*, 2013; Sanematsu & Watanabe, 2016). In the study area, a total of three weathered profiles of granitic rocks were studied, one representative outcrop from the Daroctan Granite and two representative outcrops

from the Kapoas Granitoid. The weathering profiles were divided into four different layers i.e. horizon A, B, C, and D, based on the classification by Wu *et al.* (1990). Descriptions of each sample from different outcrops are outlined below.

#### 4.1.1 Daroctan Granite

The ENS 1 samples were taken in Tenegueban located at about 16 meters above sea level (masl). The outcrop is about 5 m in height and 3.5 m in length (Fig. 2c). It was divided into five layers approximately 1 m thick each, wherein five samples (ENS 1a to 1e from top to bottom) were collected representing each layer. ENS 1a is a part of the near surface zone (horizon A). It is composed of light brown-colored porous weathered crust. The original rock texture is still visible having

residual quartz. ENS 1b is a part of the wholly weathered zone (horizon B). It is yellow-orange in color. The original minerals are less visible and are relatively homogenous. It is less porous compared to ENS 1a. ENS 1c, 1d, and 1e are collected from the sub-weathered zone (horizon C), which is composed of light yellow-orange-colored loose weathered crust. White clayey minerals, coarse-grained plagioclase, and quartz are visible. The parent rock exposed near this outcrop is granodiorite.

#### 4.1.2 Kapoas Granitoid

The examined exposures of weathered crust of the Kapoas Granitoid are all located in the Erawan area of the Bay Peak pluton. The first outcrop is observed along a deep canal at about 33 masl (Fig. 2d). Four

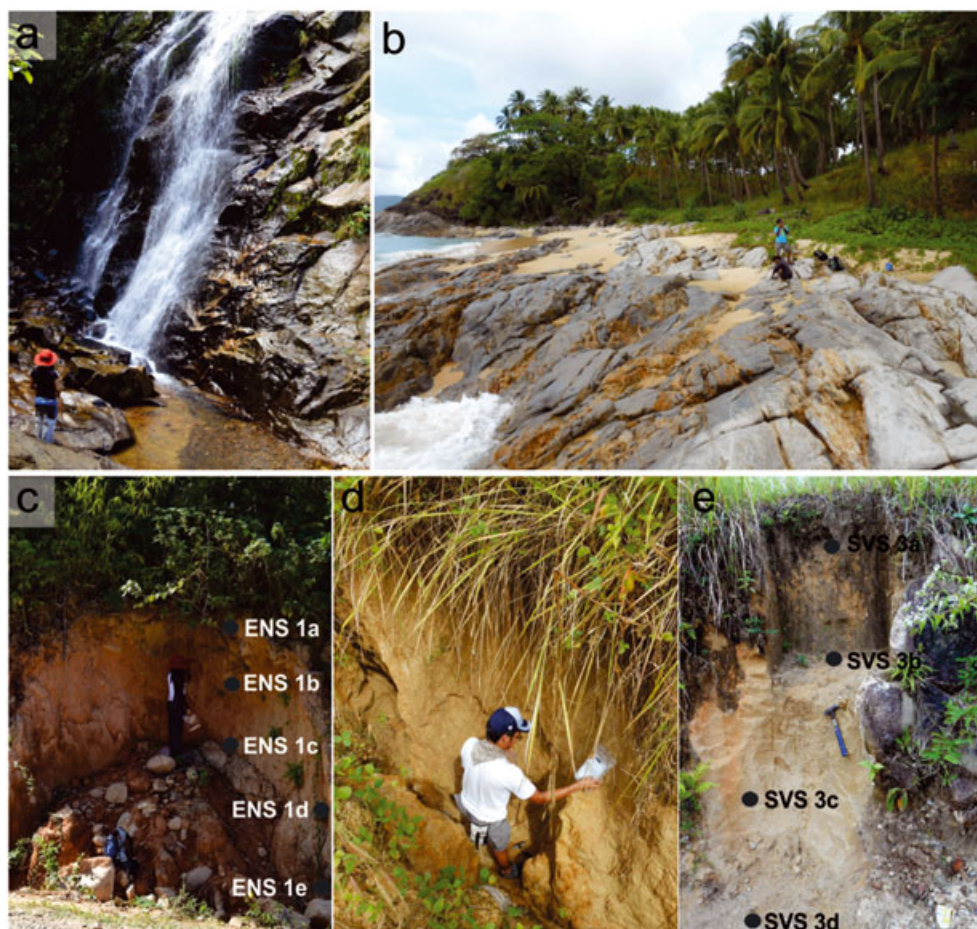


**Fig. 2** (a) Representative outcrops of the Daroctan Granite from the Barotuan pluton and the (b) Kapoas Granitoid from Ombo area, a part of the Bay Peak pluton. (c) Sampling points for the ENS 1 taken from the Tenegueban pluton of the Daroctan Granite. (d) SVS 2 and (e) SVS 3, which are both taken from the Bay Peak pluton of the Kapoas Granitoid.

samples (SVS 2a to 2d from top to bottom) from this outcrop were collected from the sub-weathered zone (horizon C) and they exhibit texture of the original rock. SVS 2a (0.25 m depth) was collected from mottled color (white to light gray and dark gray) weathered crust with visible biotite and quartz. SVS 2b (0.75 m depth) was collected from mottled color (white, pale yellow to bright brown with ilmenite grains) weathered crust. Similar to SVS 2a, quartz and mica flakes are still visible. Grain sizes of both 2a and 2b are variable. The color of sample SVS 2c (1.25 m depth) is relatively homogeneous (bright yellowish to brown). The grain sizes are also variable but are relatively smaller than the sample SVS 2a and SVS 2b. The amount of clay minerals in the sample SVS 2c is less compared to the upper profile samples. Sample SVS 2d (1.75 m depth) was collected from homogenous-colored (light gray to light yellow) weathered horizon with rough surfaces in which mica flakes is mostly visible.

Samples were also collected from another outcrop along a road cut at about 14 masl (Fig. 2e). The area is divided into four sampling points (SVS 3a to 3d from top to bottom) that are part of the wholly weathered zone (horizon B). SVS 3a (0.25 m depth) is composed of homogenous, light gray-colored fine-grained weathered rock, with visible mica flakes. Clay minerals are observable as prominent white-colored patches. SVS 3b (1.25 m depth) is similar to SVS 3a in composition with light gray color. Mica flakes are still visible with notable ilmenite grains. This sample contains fewer clays than the sample SVS 3a. Samples SVS 3c (2.25 m depth) and SVS 3d (3.25 m depth) are both pale yellow in color and contain lesser mica flakes compared to the sample SVS 3a and SVS 3b.

## 4.2 Petrography and mineralogy

Measurement of the magnetic susceptibility of granitic rocks can help in elucidating the type of granite, either magnetite or ilmenite series (Ishihara, 1977; Ishihara *et al.*, 1995). Magnetic susceptibility values of the Kapoas Granitoid range from 0.02 to  $1.23 \times 10^{-3}$  SI with a mean value of  $0.13 \times 10^{-3}$  SI. The magnetic susceptibility values of the Daroctan Granite range from 0.01 to  $0.24 \times 10^{-3}$  SI with a mean value of  $0.12 \times 10^{-3}$  SI. Based on the granite type proposed by Ishihara (1977), all the granitoids in the study area fall into ilmenite series type of granite ( $<3.0 \times 10^{-3}$  SI, Ishihara & Chappell, 2010).

The Daroctan Granite samples are holocrystalline and consist of subhedral to anhedral crystals of quartz, plagioclase, K-feldspar and biotite as the main rock-forming minerals (Fig. 3a, b). Quartz, K-feldspar, and plagioclase exhibit consertal intergrowth. Quartz is mostly subhedral to anhedral. Plagioclase is mostly subhedral and is moderately to completely replaced by sericite. Some biotite crystals are chloritized. Chlorite occurs as alteration along the rims of biotite or sometimes completely replacing biotite grains. Zircon and monazite occur as inclusions in quartz, K-feldspar, and plagioclase. Biotite contains inclusions of ilmenite and apatite. The granite host rocks and granodiorite enclaves are similar in composition and features, but the enclaves contain more opaque minerals than the host granites. Enclaves (up to 30 cm diameter) are holocrystalline, consisting mostly of subhedral to anhedral quartz, plagioclase, K-feldspar, and biotite. K-feldspar and plagioclase are more intensely altered to sericite compared to the host granites. Biotite shows skeletal structure. Chloritization of biotite is common and more intense compared to the host granites. Zircon occurs as inclusions in biotite, plagioclase, K-feldspar, and quartz. Monazite occurs as inclusions in quartz and plagioclase. Ilmenite occurs as inclusions in all other primary minerals. Small grains of cassiterite sometimes occur as intergrowth with ilmenite.

The Bay Peak pluton of the Kapoas Granitoid is composed of biotite granodiorite (Fig. 3c, d). It contains phenocrystic plagioclase from about 0.75 mm to 1.5 mm in size, which show oscillatory zoning. Quartz shows undulose extinction. Some grains of K-feldspar shows perthite and micrographic textures; however, perthite texture is not common. Plagioclase and K-feldspar are slightly altered to sericite. Most of the grains of quartz, K-feldspar, and plagioclase are anhedral to subhedral. Biotite is replaced by chlorite at the grain edges. A few grains of muscovite associated with biotite are observed in the samples of the Bay Peak granodiorite. Biotite contains ilmenite, apatite, and zircon inclusions. Some zircon inclusions are observed in quartz. Monazite occurs as inclusions in K-feldspar. Enclaves (up to 65 cm diameter) of the Bay Peak Granite are similar in composition to the granodiorite host rock. Enclaves also contain phenocrystic plagioclase from about 2 mm to 3 mm. A relatively intense sericite alteration in K-feldspar and plagioclase was observed in enclaves. Also, chlorite alteration in biotite is more prominent in the enclave. Zircon occurs in biotite and plagioclase while apatite

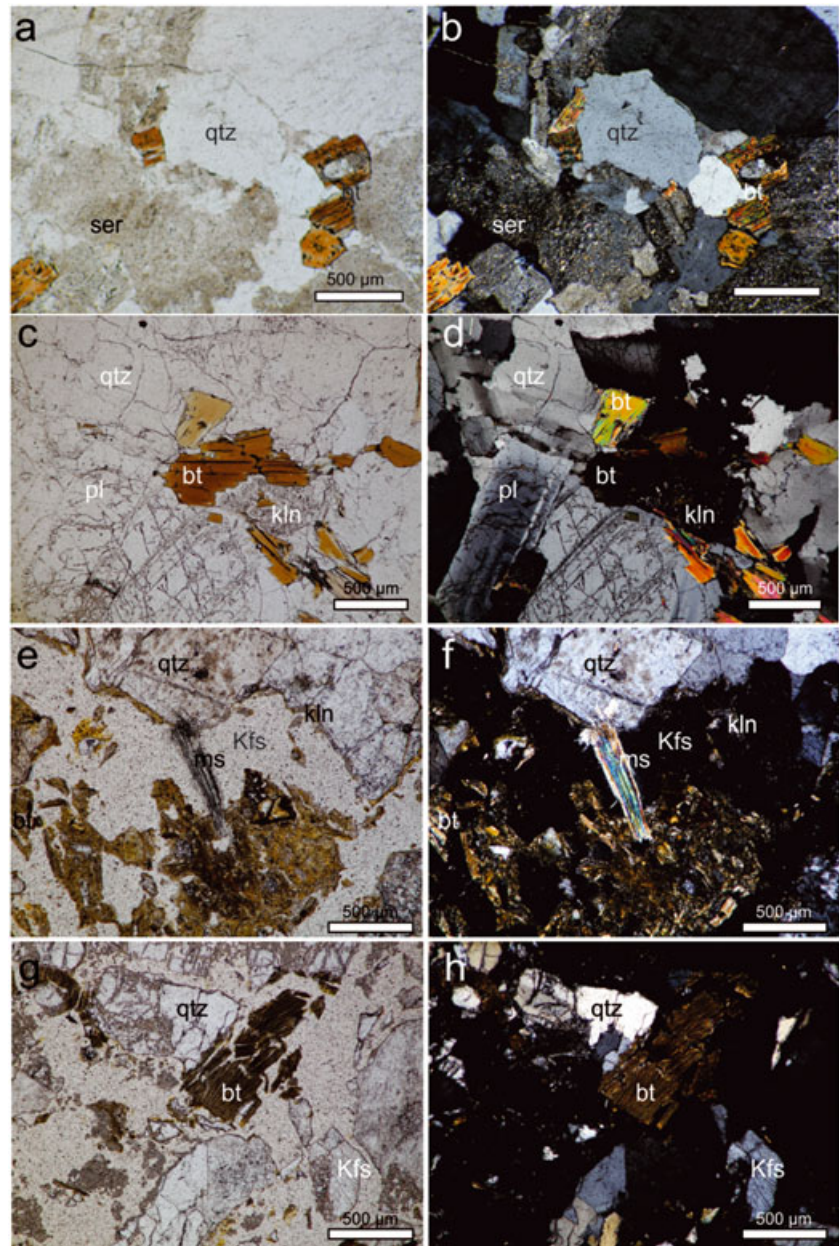


**Fig. 3** (a, b) Plane-polarized and cross-polarized photomicrographs of the biotite granite sample from the Daroctan Granite showing equigranular grains of quartz, seriate K-feldspar, and plagioclase. (c, d) Plane-polarized and cross-polarized photomicrographs of the biotite granodiorite from the Bay Peak unit of the Kapoas Granitoid. (e, f) Plane-polarized and cross-polarized photomicrographs of the Daroctan Granite and (g, h) the Kapoas Granitoid weathered crusts. Abbreviations (adopted from Siivola and Schmid, 2007): qtz, quartz; Kfs, K-feldspar; bt, biotite; ser, sericite; pl, plagioclase; kln, kaolinite; ms, muscovite.

occurs as inclusions in plagioclase. Monazite inclusions in quartz are larger than in the granodiorite host rock.

The Mt. Kapoas pluton of the Kapoas Granitoid is composed of biotite granodiorite with phenocrystic plagioclase. Quartz, K-feldspar, and plagioclase grains are mostly anhedral to subhedral. Quartz does not show undulose extinction. Some plagioclase crystals show oscillatory zoning. K-feldspar shows micrographic texture and is moderately sericitized. Biotite is partly altered to chlorite. Muscovite is also observed

to be associated with biotite crystals. Zircon and monazite occur as inclusions in quartz. Zircon also occurs as inclusions in biotite. Trace amounts of ilmenite are associated with biotite. Granodiorite enclaves in the Mt. Kapoas pluton are similar in mineralogy to the granodiorite host rock but contains equigranular crystals of quartz, K-feldspar, and plagioclase. Megascopically, enclaves appear darker than the host rock. Granodiorite enclaves contain more biotite, ilmenite, and monazite than the granodiorite

host rock. Apatite occurs as inclusions in quartz. Quartz and plagioclase contain monazite inclusions while biotite contains zircon inclusions.

Horizons B and C of the Daroctan Granite samples still contain quartz while plagioclase and K-feldspar are mostly altered to clay minerals (Fig. 3e, f). Biotite is intensely altered. Weathered crust of the Kapoas Granitoid still contains abundant quartz (Fig. 3g, h). In the top horizon (SVS 2a), plagioclase and K-feldspar are moderately to intensely altered to clay minerals. Plagioclase and K-feldspar in the bottom horizons are mostly altered to kaolinite. Biotite is altered to vermiculite. Monazite in the samples of the weathered crusts tends to be coarser than those observed in the parent granodiorite.

Clay minerals in the samples of weathered crust were identified using XRD. Clay minerals in the samples of weathered crust from the Daroctan Granite ENS 1a to 1e are mostly interstratified illite-vermiculite with approximately 10 Å d-spacing and kaolinite with approximately 7 Å d-spacing. Chlorite and kaolinite peaks overlap, thus, the absence of chlorite was confirmed by HCl treatment. Clay minerals in the samples of weathered crust from the Kapoas Granitoid samples SVS 2a to 2d are mostly kaolinite and interstratified illite-vermiculite. The sample SVS 2a also contains montmorillonite that exhibited a peak shift from 15.4 Å to 17.4 Å when treated with ethylene glycol. Clay minerals in the sample SVS 3a to 3d are only kaolinite and interstratified illite-vermiculite.

Mineralogical analysis using SEM-EDS was also carried out on samples ENS 1c and SVS 3d. The sample of the weathered crust of the Daroctan Granite contains residual REE-bearing minerals such as monazite (containing LREE i.e. La, Ce, Nd) and xenotime (containing HREE i.e. Gd, Tb, Yb, Y) (Fig. 4a,b). The sample of the weathered crust of the Kapoas Granitoid contains only monazite as REE-bearing mineral. In the beach sand, allanite (containing LREE i.e. La, Ce, Nd) was observed (Fig. 4c). Zircon is intergrown with monazite. Vermiculite occurs as fibrous grains with alternating dark and bright bands in the backscattered electron (BSE) images (Fig. 5a to e). The dark and bright bands correspond to least altered and intensely altered vermiculite, respectively. The alteration (from dark to the bright band) resulted in an increase in Al and Si contents, removal of K, and an addition of P and Cl (Fig. 5b). In another vermiculite grain, the dark bands lost Ti and K while Mn was added. Pb and Ba are enriched in the bright bands. Cerianite ( $\text{CeO}_2$ ), a secondary REE-bearing mineral, occurs at the edges

of the altered vermiculite (dark bands) (Fig. 5d). These cerianite are associated with Mn and Fe-oxides.

The sample of the weathered crust of the Kapoas Granitoid SVS 3d only contains residual monazite as a REE-bearing mineral. Similar to the sample of the weathered crust of the Daroctan Granite, it also contains vermiculite which occurs as fibrous grains with dark and bright alternating bands (Fig. 5e). Goethite was also observed. Minor Fe-rich chlorite formed at the edges of biotite (Fig. 5f). On the other hand, ilmenite in the sample is altered, manifested by substitution of Fe with Mn and increase of Ti.

### 4.3 Major elements geochemical signatures

The granitic rocks of the Daroctan Granite and Kapoas Granitoid show similar geochemical signatures (Table 1). Both units are classified as high-K calc-alkaline (Fig. 6a) (Peccerillo & Taylor, 1976), and peraluminous (Fig. 6b) (Shand, 1943) type of granitoids. Samples from these units plotted in the I- and S-types classification of Chappell and White (1974) (Fig. 6b). The  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , MgO, and CaO contents of both units are negatively correlated with  $\text{SiO}_2$  (Fig. 7a to e). The  $\text{Na}_2\text{O}$  and  $\text{P}_2\text{O}_5$  are also negatively correlated but show relatively gentler slope compared to other major elements (Fig. 7f, g). Similar trends were observed in both plutons; however the Daroctan Granite has lower  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ , and MgO contents compared to the Kapoas Granitoid.

Representative samples of weathered crusts from the Daroctan and Kapoas Granitoid are characterized by Chemical Index of Alteration (CIA, Nesbitt & Young, 1982) ranging from 72 to 90 % (Fig. 6c). The molar proportions of  $(\text{CaO} + \text{Na}_2\text{O}) - \text{Al}_2\text{O}_3 - \text{K}_2\text{O}$  of the samples show that they exhibit a mostly advanced weathering trend. Samples of weathered crust from both the Daroctan Granite and Kapoas Granitoid plot on the illite/muscovite to kaolinite field.

The behavior of major elements in the weathered crust was compared with that of the parent granitic rocks (Fig. 7) (Table 2). The  $\text{Al}_2\text{O}_3$  content of the weathered crust significantly increases, particularly in the Daroctan Granite samples. Similarly, the  $\text{Fe}_2\text{O}_3$  content also increases in the weathered crust in the Daroctan Granite samples. The  $\text{Fe}_2\text{O}_3$  content of the weathered crust in the Kapoas Granitoid is within the field of the parent granitic rocks, but the  $\text{SiO}_2$  increases slightly. The  $\text{TiO}_2$  contents of the weathered crusts in both the Daroctan Granite and Kapoas Granitoid are

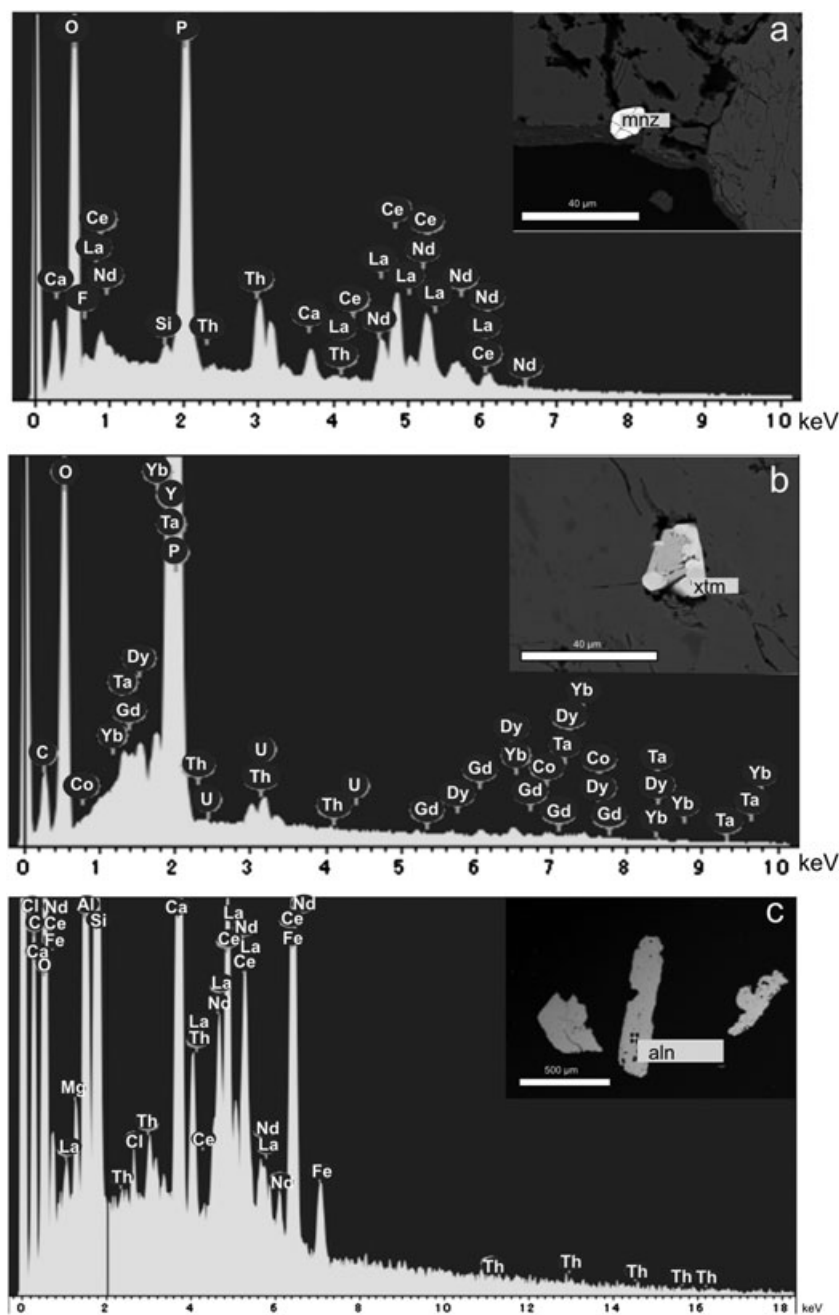


Fig. 4 Representative SEM-EDS photomicrographs and spectra of REE-bearing minerals (a) monazite and (b) xenotime from the Daroetan Granite weathered crust, and (c) allanite from the Kapoas Granitoid beach sand sample.

within the field of the parent granitic rocks, whereas the  $\text{SiO}_2$  contents increase. The  $\text{P}_2\text{O}_5$  and  $\text{CaO}$  contents slightly decrease in the weathered crusts in both plutons. The content of  $\text{MgO}$  in the weathered crusts of the Kapoas Granitoid does not change from the parent granitic rocks while  $\text{MgO}/\text{SiO}_2$  ratio in the weathered crust of the Daroetan Granite decreases. The  $\text{Na}_2\text{O}$  contents of the weathered crusts significantly decrease in both units.

#### 4.4 REE concentration

The REE contents of the Daroetan Granite fresh rock samples range from about 80 to 143 ppm, with a mean value of 115 ppm. The REE contents of the Kapoas Granitoid range from 53 to 243 ppm, with a mean value of 137 ppm. In the chondrite-normalized REE plot (McDonough & Sun, 1995) (Fig. 8), LREE are enriched in the Kapoas Granitoid compared to the

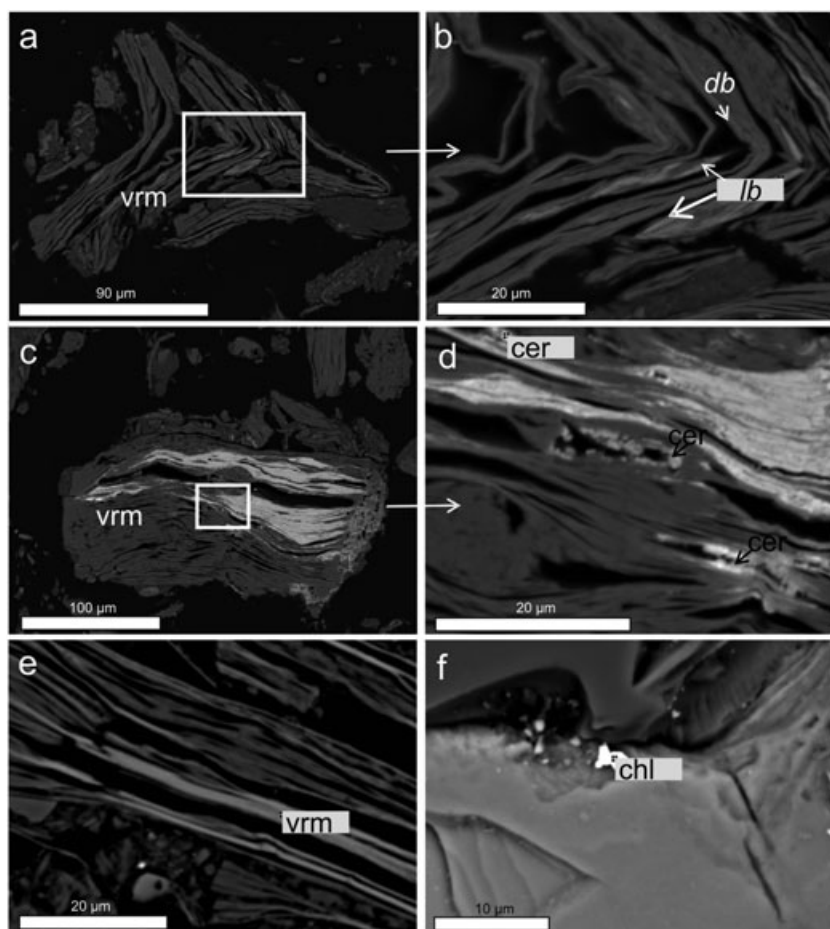


**Fig. 5** SEM-EDS photomicrographs showing (a) vermiculite grain from the Daroctan Granite weathered crust with minor alteration as indicated by the relatively small changes in the dark bands and light bands. (b) Alteration includes an increase in Al and Si-content, removal of K, and addition of P and Cl. (c) Vermiculite grain showing light and dark bands and contains (d) cerianite at the edges. (e) Vermiculite in the Kapoas Granitoid also occurs as fibrous grains with dark and bright alternating bands. (f) Fe-rich chlorite formed at the edges of biotite. Abbreviations (adopted from Siivola and Schmid, 2007): mnz, monazite; xtm, xenotime; vrm, vermiculite; db, dark band; lb, light band; cer, cerianite; chl, chlorite.

Daroctan Granite. Negative Eu anomaly ( $\text{Eu}/\text{Eu}^* = \text{Eu}_N/(\text{Sm}_N \times \text{Gd}_N)^{1/2}$ ) is significant in the Daroctan Granite (about 0.08 to 0.54) than in the Kapoas Granitoid fresh rock samples (0.32 to 1.35).

Streams sediments from Erawan, Ombo, and Mt. Kapoas for the Kapoas Granitoid and tributaries in Bulalacao and Nagkaletkalet for the Daroctan Granite were analyzed (Table 2). Beach sands along Ombo Beach containing heavy minerals were also analyzed. The REE contents of the stream sediments in the Kapoas Granitoid range from 93.3 to 5,208 ppm with a mean value of 1,392 ppm. The REE contents of two sand samples from Ombo Beach are 432 to 5208 ppm with with an average value of 2820 ppm. One particular beach sand in the Ombo Beach with heavy minerals accumulation, such as monazite and allanite, contain LREEs such as La, Ce, Nd and Sm up to >10,000 ppm. The Th and U contents of this sample are also elevated compared to other areas, >1,000 and 83.7 ppm, respectively. This area is located near Imuruan

Bay where high Th and U radiometric anomalies were observed (Ringis *et al.*, 1993). The REE contents of the stream sediments derived from the Daroctan Granite are not elevated, only 40.5 to 53.8 ppm with a mean value of 47.2 ppm.

The chondrite-normalized (McDonough & Sun, 1995) REE values of the weathered granitic crusts, stream sediments, and beach sands are shown in Fig. 7. REE of the Daroctan Granite stream sediments are relatively depleted compared to both the parent granite and the weathered crusts. On the other hand, REE are enriched in the weathered granites, particularly the LREE content, compared to the parent granite. The Eu anomalies of the Daroctan Granite are steeper than Eu anomalies of the Kapoas Granitoid, with values ranging from 0.47 to 0.51. The Ce anomalies of the Daroctan Granite differ per horizon, with values ranging from 0.58 to 1.05. The sub-weathered zone ENS 1d in Daroctan show positive Ce anomaly while negative Ce anomalies are apparent in the remaining

**Table 1** Major and trace elements composition of the Daroatan Granite and the Kapoas Granitoid

|                                | Daroatan Granite |               |              |               | EN11          | EN12         | EN13b         | EN15          | EN17          | EN18          | EN19          | EN20          | EN21          | Kapoas Granitoid |               | SV4           |
|--------------------------------|------------------|---------------|--------------|---------------|---------------|--------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|------------------|---------------|---------------|
|                                | EN2              | EN4           | EN8a         |               |               |              |               |               |               |               |               |               |               | SV51             | SV2           |               |
| SiO <sub>2</sub> (%)           | 75.3             | 71.9          | 70.8         | 69.1          | 69.1          | 69.9         | 70.4          | 69.6          | 76.8          | 68.4          | 71            | 69.6          | 75.0          | 67.0             | 69.3          | 68.8          |
| TiO <sub>2</sub>               | 0.19             | 0.37          | 0.48         | 0.51          | 0.51          | 0.44         | 0.50          | 0.47          | 0.13          | 0.42          | 0.37          | 0.38          | 0.24          | 0.57             | 0.53          | 0.59          |
| Al <sub>2</sub> O <sub>3</sub> | 12.6             | 13.9          | 13.9         | 14.5          | 14.5          | 14.4         | 13.9          | 15.0          | 12.4          | 15.1          | 14.1          | 14.5          | 12.7          | 15.9             | 14.9          | 15.6          |
| Fe <sub>2</sub> O <sub>3</sub> | 2.08             | 3.13          | 3.20         | 3.65          | 3.65          | 3.50         | 3.72          | 2.94          | 1.50          | 3.77          | 3.24          | 3.56          | 2.15          | 3.92             | 3.04          | 3.32          |
| MnO                            | 0.03             | 0.05          | 0.06         | 0.06          | 0.06          | 0.05         | 0.06          | 0.05          | 0.01          | 0.06          | 0.05          | 0.05          | 0.04          | 0.06             | 0.05          | 0.05          |
| MgO                            | 0.29             | 0.85          | 1.15         | 1.28          | 1.28          | 1.36         | 1.24          | 1.27          | 0.13          | 1.34          | 1.09          | 1.23          | 0.40          | 1.59             | 1.75          | 1.90          |
| CaO                            | 0.28             | 2.16          | 2.70         | 2.94          | 2.94          | 2.91         | 1.25          | 2.88          | 0.16          | 2.18          | 1.87          | 2.87          | 0.79          | 1.87             | 2.69          | 3.23          |
| Na <sub>2</sub> O              | 2.43             | 3.47          | 2.97         | 3.27          | 3.27          | 3.07         | 3.17          | 3.24          | 2.72          | 3.69          | 3.34          | 3.36          | 2.84          | 3.10             | 3.21          | 3.59          |
| K <sub>2</sub> O               | 5.92             | 3.66          | 3.72         | 3.47          | 3.47          | 3.39         | 3.97          | 3.26          | 5.22          | 3.31          | 3.86          | 3.46          | 4.59          | 4.64             | 4.08          | 3.10          |
| P <sub>2</sub> O <sub>5</sub>  | 0.13             | 0.07          | 0.10         | 0.10          | 0.10          | 0.09         | 0.11          | 0.11          | 0.05          | 0.10          | 0.09          | 0.09          | 0.12          | 0.27             | 0.16          | 0.18          |
| LOI                            | 0.69             | 0.50          | 0.92         | 1.12          | 1.12          | 0.91         | 1.73          | 1.13          | 0.87          | 1.72          | 0.94          | 0.91          | 1.09          | 1.08             | 0.29          | 0.23          |
| <b>Total</b>                   | <b>100.00</b>    | <b>100.01</b> | <b>99.99</b> | <b>100.00</b> | <b>100.00</b> | <b>99.98</b> | <b>100.00</b> | <b>100.00</b> | <b>100.00</b> | <b>100.01</b> | <b>100.00</b> | <b>100.00</b> | <b>100.01</b> | <b>100.00</b>    | <b>100.02</b> | <b>100.00</b> |
| Y (ppm)                        | 27.9             | 40.4          | 20.7         | 21.9          | 26            | 26           | 24.6          | 23.8          | 43            | 24.4          | 26.1          | 25.6          | 27.2          | 33.7             | 19.3          | 15            |
| U                              | 5.53             | 5.30          | 2.51         | 3.57          | 2.84          | 2.84         | 4.12          | 4.73          | 5.76          | 4.70          | 5.55          | 5.39          | 5.08          | 6.98             | 4.01          | 3.37          |
| Th                             | 10.4             | 13.5          | 13.5         | 13.4          | 12.4          | 12.4         | 11.9          | 13.8          | 15.5          | 11.3          | 13.5          | 13.1          | 9.75          | 15.1             | 11.9          | 11.6          |
| La                             | 13.6             | 25.8          | 25.8         | 25.9          | 23.9          | 23.9         | 22.6          | 25.9          | 19.2          | 20.4          | 23.8          | 24            | 15            | 53               | 37.9          | 29.5          |
| Ce                             | 29.7             | 53.8          | 52.2         | 51.9          | 49            | 49           | 44.8          | 49.6          | 37.2          | 40.9          | 49.8          | 50.8          | 31.2          | 100              | 64.2          | 56.9          |
| Pr                             | 3.55             | 6.63          | 6.15         | 6.11          | 5.84          | 5.84         | 5.38          | 6.13          | 5.11          | 4.96          | 5.97          | 6.08          | 3.75          | 11.85            | 8.10          | 6.52          |
| Nd                             | 12.9             | 25.1          | 22.1         | 22.2          | 21.5          | 21.5         | 19.8          | 22.8          | 18.8          | 18.9          | 22.2          | 22.4          | 14            | 44.4             | 29.6          | 22.9          |
| Sm                             | 3.57             | 6.27          | 4.67         | 4.58          | 4.74          | 4.74         | 4.64          | 4.88          | 5.18          | 4.54          | 4.84          | 5.22          | 3.66          | 9.82             | 6.22          | 4.56          |
| Eu                             | 0.35             | 0.65          | 0.74         | 0.74          | 0.67          | 0.67         | 0.77          | 0.83          | 0.15          | 0.66          | 0.68          | 0.63          | 0.48          | 0.96             | 1.47          | 1.02          |
| Gd                             | 3.56             | 5.90          | 4.21         | 4.09          | 4.48          | 4.48         | 4.39          | 4.43          | 5.55          | 4.25          | 4.63          | 4.59          | 3.63          | 8.42             | 5.37          | 3.91          |
| Tb                             | 0.71             | 1.02          | 0.64         | 0.65          | 0.75          | 0.75         | 0.71          | 0.66          | 1.03          | 0.69          | 0.74          | 0.75          | 0.71          | 1.24             | 0.82          | 0.51          |
| Dy                             | 4.71             | 6.55          | 3.65         | 3.62          | 4.31          | 4.31         | 4.34          | 3.71          | 6.79          | 4.24          | 4.34          | 4.27          | 4.46          | 6.72             | 4.33          | 2.86          |
| Ho                             | 0.97             | 1.38          | 0.69         | 0.78          | 0.88          | 0.88         | 0.91          | 0.83          | 1.45          | 0.87          | 0.89          | 0.88          | 0.92          | 1.24             | 0.81          | 0.52          |
| Er                             | 2.80             | 4.10          | 1.95         | 2.21          | 2.59          | 2.59         | 2.69          | 2.11          | 4.20          | 2.50          | 2.57          | 2.48          | 2.57          | 2.85             | 2.00          | 1.39          |
| Tm                             | 0.43             | 0.64          | 0.33         | 0.31          | 0.39          | 0.39         | 0.39          | 0.36          | 0.73          | 0.37          | 0.37          | 0.37          | 0.42          | 0.41             | 0.31          | 0.20          |
| Yb                             | 2.88             | 4.14          | 2.04         | 2.15          | 2.43          | 2.43         | 2.50          | 2.33          | 4.15          | 2.52          | 2.60          | 2.64          | 2.52          | 2.28             | 1.85          | 1.31          |
| Lu                             | 0.36             | 0.58          | 0.29         | 0.30          | 0.34          | 0.34         | 0.43          | 0.31          | 0.65          | 0.32          | 0.35          | 0.37          | 0.39          | 0.29             | 0.26          | 0.18          |
| LREE                           | 63.7             | 118.3         | 111.7        | 111.4         | 105.7         | 105.7        | 97.9          | 110.1         | 85.6          | 90.4          | 107.3         | 109.1         | 68.1          | 220.0            | 147.5         | 121.4         |
| HREE                           | 16.4             | 24.3          | 13.8         | 14.1          | 16.2          | 16.2         | 16.4          | 14.7          | 24.6          | 15.8          | 16.5          | 16.4          | 15.6          | 23.5             | 15.8          | 10.9          |
| <b>REE</b>                     | <b>80.1</b>      | <b>142.6</b>  | <b>125.5</b> | <b>125.5</b>  | <b>121.8</b>  | <b>121.8</b> | <b>114.4</b>  | <b>124.9</b>  | <b>110.2</b>  | <b>106.1</b>  | <b>123.8</b>  | <b>125.5</b>  | <b>83.7</b>   | <b>243.5</b>     | <b>163.2</b>  | <b>132.3</b>  |
| Eu/Eu*                         | 0.30             | 0.33          | 0.51         | 0.52          | 0.44          | 0.44         | 0.52          | 0.54          | 0.09          | 0.46          | 0.44          | 0.39          | 0.40          | 0.32             | 0.78          | 0.74          |
| Ce/Ce*                         | 1.03             | 1.00          | 1.00         | 1.00          | 1.00          | 1.00         | 0.98          | 0.95          | 0.91          | 0.98          | 1.01          | 1.02          | 1.01          | 0.97             | 0.89          | 0.99          |
|                                | SV6              | SV9           | SV16         | SV23a         | SV26          | SV26         | SV33          | SV43          | SV44          | SV45          | SV46a         | SV47          | SV49          | SV50             |               |               |
| SiO <sub>2</sub> (%)           | 69.5             | 68.7          | 65.5         | 70.5          | 68.4          | 68.4         | 68.5          | 72.1          | 77.89         | 70.4          | 71.4          | 68.8          | 68.3          | 68.8             |               |               |
| TiO <sub>2</sub>               | 0.55             | 0.59          | 0.73         | 0.49          | 0.57          | 0.57         | 0.63          | 0.37          | 0.57          | 0.47          | 0.42          | 0.58          | 0.67          | 0.56             |               |               |
| Al <sub>2</sub> O <sub>3</sub> | 15.0             | 15.3          | 16.1         | 14.8          | 15.5          | 15.5         | 14.7          | 14.4          | 15.2          | 14.5          | 14.3          | 14.9          | 15.6          | 15.9             |               |               |
| Fe <sub>2</sub> O <sub>3</sub> | 2.99             | 3.10          | 4.03         | 2.40          | 3.14          | 3.14         | 3.68          | 2.08          | 2.93          | 2.49          | 2.33          | 3.02          | 3.39          | 2.68             |               |               |
| MnO                            | 0.05             | 0.05          | 0.06         | 0.04          | 0.05          | 0.05         | 0.07          | 0.03          | 0.06          | 0.04          | 0.04          | 0.05          | 0.05          | 0.04             |               |               |

Table 1. (Continued)

|                               | Daroctan Granite |              |              | EN11        | EN12          | EN13b        | EN15          | EN17        | EN18          | EN19          | EN20          | EN21          | Kapoa Granitoid |     | SV4 |
|-------------------------------|------------------|--------------|--------------|-------------|---------------|--------------|---------------|-------------|---------------|---------------|---------------|---------------|-----------------|-----|-----|
|                               | EN2              | EN4          | EN8a         |             |               |              |               |             |               |               |               |               | SV51            | SV2 |     |
| MgO                           | 1.81             | 1.94         | 2.56         | 1.68        | 1.90          | 2.74         | 0.82          | 2.08        | 1.62          | 1.52          | 1.96          | 1.91          | 1.56            |     |     |
| CaO                           | 3.01             | 2.77         | 3.38         | 2.54        | 3.06          | 2.82         | 1.15          | 2.64        | 2.29          | 2.20          | 2.82          | 3.05          | 2.84            |     |     |
| Na <sub>2</sub> O             | 3.42             | 3.28         | 3.62         | 3.37        | 3.51          | 2.90         | 2.95          | 3.31        | 2.96          | 3.21          | 3.10          | 3.60          | 3.83            |     |     |
| K <sub>2</sub> O              | 3.12             | 3.71         | 3.23         | 3.78        | 3.30          | 3.45         | 4.86          | 3.89        | 4.64          | 4.10          | 4.11          | 2.69          | 3.21            |     |     |
| P <sub>2</sub> O <sub>5</sub> | 0.16             | 0.16         | 0.20         | 0.14        | 0.15          | 0.15         | 0.13          | 0.16        | 0.14          | 0.12          | 0.16          | 0.18          | 0.16            |     |     |
| LOI                           | 0.42             | 0.41         | 0.54         | 0.25        | 0.43          | 0.40         | 1.16          | 0.55        | 0.42          | 0.37          | 0.40          | 0.68          | 0.42            |     |     |
| <b>Total</b>                  | <b>100.01</b>    | <b>100</b>   | <b>100</b>   | <b>100</b>  | <b>100.01</b> | <b>100</b>   | <b>100.02</b> | <b>100</b>  | <b>100.03</b> | <b>100.01</b> | <b>100.01</b> | <b>100.03</b> | <b>100</b>      |     |     |
| Y (ppm)                       | 11.1             | 13.1         | 13           | 10.3        | 14            | 15.1         | 11.1          | 12.9        | 8.1           | 9.6           | 15.9          | 13.4          | 10.9            |     |     |
| U                             | 5.49             | 3.99         | 3.57         | 2.61        | 3.17          | 2.20         | 5.07          | 3.76        | 4.62          | 4.32          | 5.37          | 5.36          | 7.48            |     |     |
| Th                            | 15.5             | 11           | 12.9         | 8.44        | 13.8          | 11.5         | 13.7          | 9.22        | 11.9          | 13.1          | 14.5          | 11.4          | 14.7            |     |     |
| La                            | 15.9             | 34.2         | 34           | 21.7        | 39.7          | 33.3         | 34.3          | 16.9        | 10.5          | 41.8          | 31.2          | 22.7          | 46.3            |     |     |
| Ce                            | 31.4             | 62.8         | 62.7         | 42.2        | 74.9          | 61.3         | 65.2          | 33.7        | 19.9          | 73.4          | 57            | 42.9          | 83.9            |     |     |
| Pr                            | 3.69             | 7.15         | 7.16         | 4.86        | 8.50          | 7.06         | 7.26          | 4.11        | 2.52          | 7.84          | 6.47          | 5             | 9.19            |     |     |
| Nd                            | 13.7             | 25.8         | 26.2         | 18.2        | 29.5          | 26.7         | 24.5          | 15.7        | 10.5          | 27.4          | 23            | 18.3          | 32.4            |     |     |
| Sm                            | 3.17             | 5.12         | 4.94         | 3.63        | 5.12          | 5.08         | 4.62          | 3.61        | 2.56          | 4.66          | 4.31          | 4.08          | 5.65            |     |     |
| Eu                            | 0.90             | 1.02         | 1.18         | 0.93        | 1.01          | 1.13         | 0.95          | 0.96        | 1             | 0.98          | 1.13          | 1.04          | 0.95            |     |     |
| Gd                            | 2.90             | 3.75         | 4.01         | 2.85        | 3.75          | 4.02         | 3.06          | 3.62        | 1.99          | 3.48          | 3.72          | 3.41          | 3.98            |     |     |
| Tb                            | 0.43             | 0.46         | 0.45         | 0.37        | 0.52          | 0.51         | 0.45          | 0.46        | 0.26          | 0.41          | 0.52          | 0.48          | 0.45            |     |     |
| Dy                            | 2.22             | 2.65         | 2.69         | 2.01        | 2.68          | 2.91         | 2.24          | 2.42        | 1.72          | 1.93          | 2.71          | 2.57          | 2.13            |     |     |
| Ho                            | 0.41             | 0.46         | 0.54         | 0.36        | 0.48          | 0.55         | 0.43          | 0.39        | 0.30          | 0.35          | 0.56          | 0.48          | 0.39            |     |     |
| Er                            | 1.10             | 1.12         | 1.18         | 0.94        | 1.29          | 1.51         | 1.10          | 1.24        | 0.70          | 0.73          | 1.43          | 1.16          | 0.83            |     |     |
| Tm                            | 0.15             | 0.20         | 0.21         | 0.13        | 0.23          | 0.21         | 0.16          | 0.22        | 0.13          | 0.14          | 0.27          | 0.20          | 0.15            |     |     |
| Yb                            | 1.02             | 1.16         | 1.27         | 0.91        | 1.34          | 1.30         | 1.06          | 1.19        | 0.76          | 0.79          | 1.66          | 1.15          | 0.94            |     |     |
| Lu                            | 0.13             | 0.19         | 0.16         | 0.13        | 0.17          | 0.19         | 0.14          | 0.16        | 0.10          | 0.11          | 0.24          | 0.20          | 0.16            |     |     |
| LREE                          | 68.8             | 136.1        | 136.2        | 91.5        | 158.7         | 134.6        | 136.8         | 74.9        | 46.9          | 156.1         | 123.1         | 94.0          | 178.4           |     |     |
| HREE                          | 8.36             | 9.99         | 10.51        | 7.70        | 10.46         | 11.20        | 8.64          | 9.70        | 5.96          | 7.94          | 11.11         | 9.65          | 9.03            |     |     |
| <b>REE</b>                    | <b>77.1</b>      | <b>146.1</b> | <b>146.7</b> | <b>99.2</b> | <b>169.2</b>  | <b>145.8</b> | <b>145.5</b>  | <b>84.7</b> | <b>52.9</b>   | <b>164.0</b>  | <b>134.2</b>  | <b>103.7</b>  | <b>187.4</b>    |     |     |
| Eu/Eu*                        | 0.90             | 0.71         | 0.81         | 0.88        | 0.70          | 0.76         | 0.77          | 0.81        | 1.35          | 0.74          | 0.86          | 0.85          | 0.61            |     |     |
| Ce/Ce*                        | 0.99             | 0.97         | 0.97         | 0.99        | 0.99          | 0.97         | 1             | 0.98        | 0.94          | 0.98          | 0.97          | 0.97          | 0.98            |     |     |

Total Fe content is expressed as  $\text{Fe}_2\text{O}_3$ .  $\text{Eu}/\text{Eu}^* = \text{Eu}_\text{N}/(\text{Sm}_\text{N} \times \text{Gd}_\text{N})^{1/2}$ ,  $\text{Ce}/\text{Ce}^* = \text{Ce}/\text{Ce}_\text{N}/(\text{La}_\text{N} \times \text{Pr}_\text{N})^{1/2}$ .

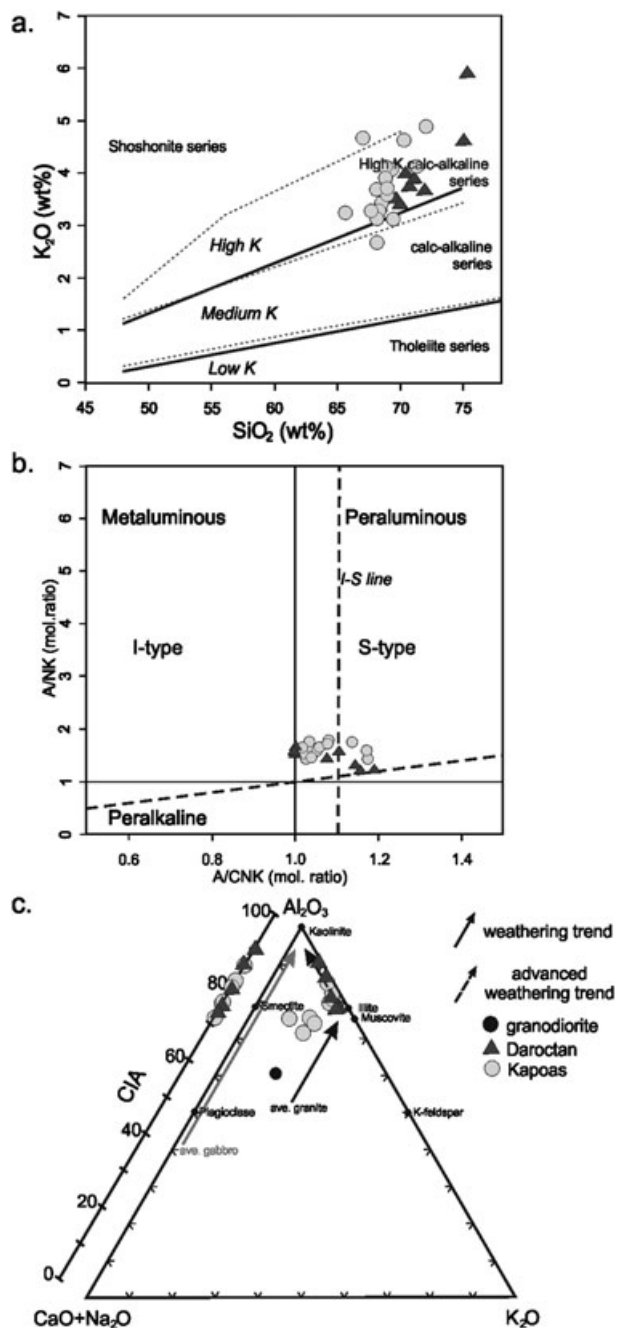


Fig. 6 Major elements discrimination diagrams showing the similar classification, such as (a) high K calc-alkaline (Peccherillo & Taylor, 1976), (b) intermediate I- and S-type, and peraluminous (Shand, 1943; Chappell & White, 1974), for both the Daroactan Granite and the Kapoas Granitoid. (c) CIA values and degree of weathering (in mol. Ratio) for the weathered granitic crusts of both unit (Nesbitt & Young, 1982).

ENS 1 weathered crust samples of the Daroactan Granite.

The LREE are more enriched in stream sediments and beach sands in Ombo and Erawan of the Kapoas Granitoid compared to other areas, even when compared to the parent granite. The weathered crust samples are also characterized by slight negative Eu anomalies ranging from 0.74 to 1.19. Compared to the parent granodiorite samples, LREE are depleted in the weathered crusts. The Ce anomaly ( $Ce/Ce^* = Ce_N/(La_N \times Pr_N)^{1/2}$ ) ranges from 0.31 to 0.93. Thus, these samples are characterized by slight negative Ce anomalies.

#### 4.5 Sequential extraction of REE from the weathered crusts

The mode of occurrence of the REE is elucidated by sequential extraction experiment. Samples selected are representative from different sampling locations in the study areas. From about 37 to 56 ppm of the  $\Sigma$ REE are extracted from the SVS 2 weathered crust sample of the Kapoas Granitoid (Table 3). On the other hand, the  $\Sigma$ REE extracted from the SVS 3 weathered crust sample from the Kapoas Granitoid ranges from 23 to 54 ppm (Table 3).  $\Sigma$ REE extracted from sample ENS 1 weathered crust from the Daroactan Granite range from 114 to 191 ppm (Table 3). The percentages of the extracted  $\Sigma$ REE from the SVS 2 and SVS 3 samples of the Kapoas Granitoid relative to the  $\Sigma$ REE of the original sample, range from 28 to 30 % and 18 to 38 %, respectively. 55 to 74 %  $\Sigma$ REE are present as extractable form in the Daroactan Granite weathered granitic rock sample.

The  $\Sigma$ REE of the weathered crusts samples of the Daroactan Granite are relatively high compared to the weathered crusts of the Kapoas Granitoid samples. The sequential extraction result shows that a significant fraction of the REE occurs as ion exchangeable, crystalline Fe-oxide occluded, and organically-bound forms. A large percentage of REE of the weathered crust samples from the Daroactan Granite samples are present as ion exchangeable (Step 2) except for Ce. A negative Ce anomaly in the leachate is the most common characteristic. Moreover, Sm and sometimes Eu exhibit negative anomaly in the ion exchangeable form. The remaining Ce were present as crystalline Fe-oxide occluded (Step 8), organically-bound (Step 6), and amorphous Fe oxide-occluded (Step 7). The remaining Eu and Gd are also present as Mn-oxide

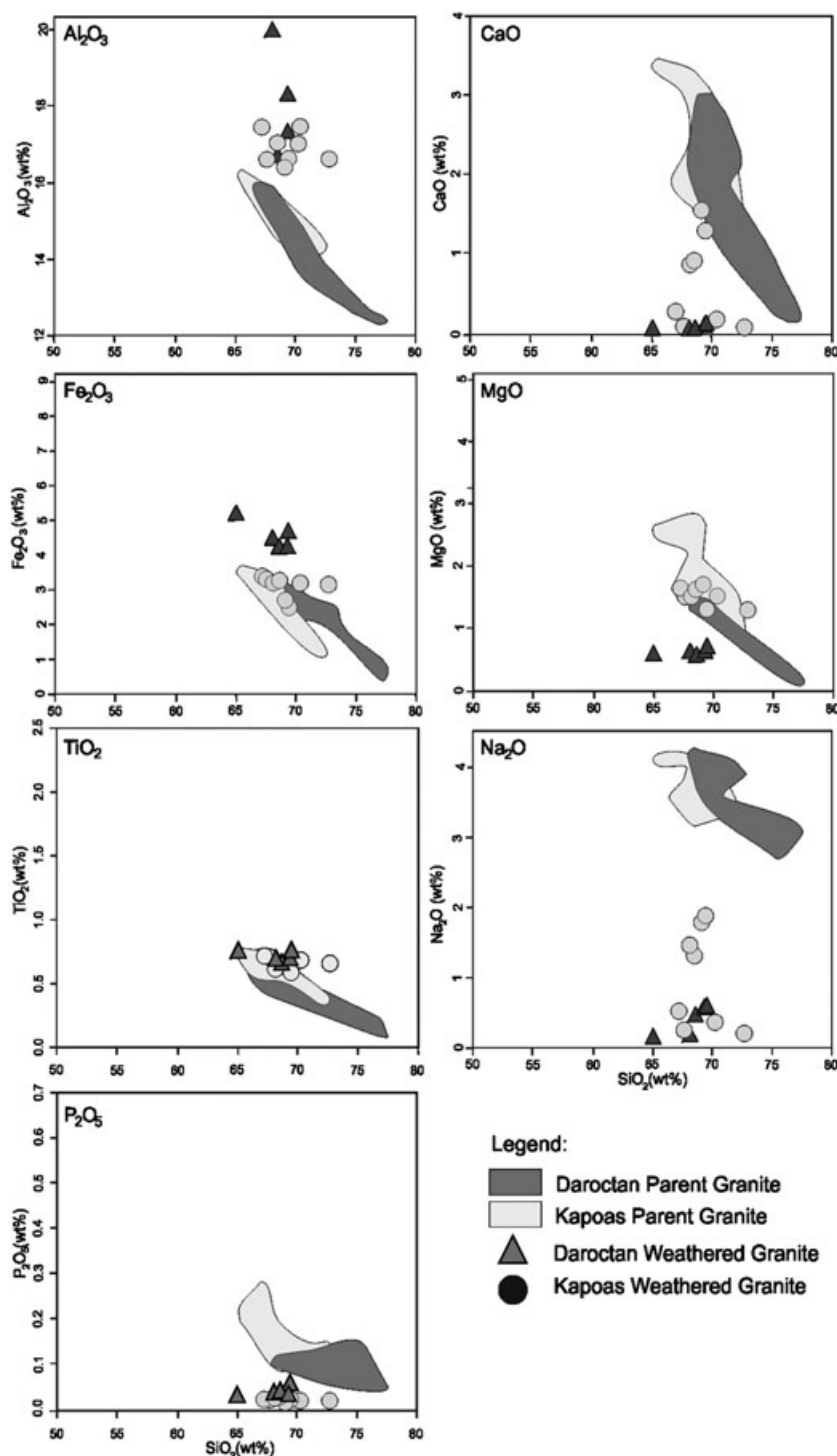


Fig. 7 Harker diagram showing trends for the major elements contents of the parent granitic rocks and their weathered crusts.

occluded (Step 5) and acid soluble (Step 4). In the weathered crusts of the Kapoas Granitoid samples SVS 2 and SVS 3, the behavior of leaching is different from that of the weathered crusts of the Daroetan

Granite. Although a large percentage of REE were also present as ion-exchangeable state, the leachate was mostly enriched in HREE. The pattern is also slightly different among the various samples, wherein only

**Table 2** Weathered granitic crust and stream sediments major and trace elements data

| Sample                     | SiO <sub>2</sub> (%) | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MnO   | MgO  | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> | LOI   | Total |      |      |      |       |      |        |    |      |      |      |      |      |       |
|----------------------------|----------------------|------------------|--------------------------------|--------------------------------|-------|------|------|-------------------|------------------|-------------------------------|-------|-------|------|------|------|-------|------|--------|----|------|------|------|------|------|-------|
| SVS2a                      | 69.2                 | 0.67             | 16.6                           | 2.70                           | 0.03  | 1.71 | 1.56 | 1.78              | 2.08             | 0.02                          | 3.82  | 100.2 | REE  | U    | Th   | Y     | Lu   | Yb     | Tm |      |      |      |      |      |       |
| SVS2b                      | 69.5                 | 0.59             | 16.4                           | 2.49                           | 0.03  | 1.31 | 1.30 | 1.88              | 3.34             | 0.02                          | 3.40  | 100.2 |      |      |      |       |      |        |    | 1.32 | 0.19 | 18.1 | 13.7 | 5.38 | 143.3 |
| SVS2c                      | 68.6                 | 0.63             | 16.6                           | 3.24                           | 0.04  | 1.63 | 0.93 | 1.31              | 3.56             | 0.03                          | 4.23  | 100.8 |      |      |      |       |      |        |    | 1.23 | 0.18 | 13.3 | 11.4 | 5.61 | 134.0 |
| SVS2d                      | 68.2                 | 0.62             | 17.0                           | 3.21                           | 0.04  | 1.51 | 0.86 | 1.46              | 3.16             | 0.02                          | 4.69  | 100.7 |      |      |      |       |      |        |    | 1.63 | 0.24 | 15.5 | 11.6 | 4.71 | 129.5 |
| SVS3a                      | 67.3                 | 0.72             | 17.3                           | 3.38                           | 0.04  | 1.65 | 0.29 | 0.52              | 3.62             | 0.02                          | 5.21  | 100.0 |      |      |      |       |      |        |    | 2.50 | 0.32 | 29.8 | 13.9 | 6.26 | 190.6 |
| SVS3b                      | 70.3                 | 0.69             | 17.4                           | 3.19                           | 0.04  | 1.55 | 0.17 | 0.36              | 3.63             | 0.02                          | 5.20  | 102.6 |      |      |      |       |      |        |    | 0.52 | 0.08 | 7.10 | 7.26 | 1.66 | 93.5  |
| SVS3c                      | 67.7                 | 0.71             | 17                             | 3.30                           | 0.04  | 1.52 | 0.10 | 0.25              | 3.30             | 0.02                          | 5.58  | 99.5  |      |      |      |       |      |        |    | 1.44 | 0.21 | 17   | 9.95 | 3.23 | 135.7 |
| SVS3d                      | 72.7                 | 0.66             | 16.6                           | 3.14                           | 0.03  | 1.31 | 0.09 | 0.20              | 2.64             | 0.02                          | 5.71  | 103.1 |      |      |      |       |      |        |    | 1.32 | 0.19 | 18.1 | 13.7 | 5.38 | 143.3 |
| ENS1a                      | 65.0                 | 0.76             | 21.6                           | 5.17                           | 0.03  | 0.61 | 0.07 | 0.14              | 2.09             | 0.03                          | 8.34  | 103.9 |      |      |      |       |      |        |    | 1.23 | 0.18 | 13.3 | 11.4 | 5.61 | 134.0 |
| ENS1b                      | 68.1                 | 0.69             | 19.9                           | 4.51                           | 0.03  | 0.62 | 0.09 | 0.19              | 2.87             | 0.04                          | 6.70  | 103.9 |      |      |      |       |      |        |    | 1.63 | 0.24 | 15.5 | 11.6 | 4.71 | 129.5 |
| ENS1c                      | 69.3                 | 0.70             | 18.0                           | 4.27                           | 0.04  | 0.65 | 0.11 | 0.57              | 3.68             | 0.04                          | 5.56  | 103.2 |      |      |      |       |      |        |    | 2.50 | 0.32 | 29.8 | 13.9 | 6.26 | 190.6 |
| ENS1d                      | 68.6                 | 0.66             | 16.7                           | 4.25                           | 0.03  | 0.59 | 0.10 | 0.46              | 4.05             | 0.04                          | 5.10  | 100.6 |      |      |      |       |      |        |    | 0.52 | 0.08 | 7.10 | 7.26 | 1.66 | 93.5  |
| ENS1e                      | 69.5                 | 0.76             | 17.3                           | 4.71                           | 0.06  | 0.72 | 0.12 | 0.59              | 4.25             | 0.06                          | 4.92  | 102.9 |      |      |      |       |      |        |    | 1.44 | 0.21 | 17   | 9.95 | 3.23 | 135.7 |
| (ppm)                      |                      | Ce               | Pr                             | Nd                             | Sm    | Eu   | Gd   | Tb                | Dy               | Ho                            | Er    | Tm    |      |      |      |       |      |        |    | Yb   | Lu   | Y    | Th   | U    | REE   |
| SVS2a                      | 36.4                 | 55.4             | 7.53                           | 26.7                           | 5.05  | 1.09 | 3.98 | 0.55              | 2.99             | 0.55                          | 1.33  | 0.21  |      |      |      |       |      |        |    | 1.32 | 0.19 | 18.1 | 13.7 | 5.38 | 143.3 |
| SVS2b                      | 32                   | 56.3             | 6.57                           | 24                             | 4.38  | 1.08 | 3.59 | 0.45              | 2.32             | 0.47                          | 1.28  | 0.19  | 1.23 | 0.18 | 13.3 | 11.4  | 5.61 | 134.0  |    |      |      |      |      |      |       |
| SVS2c                      | 29.4                 | 52.5             | 6.53                           | 23.6                           | 4.76  | 1.16 | 3.77 | 0.54              | 3.06             | 0.54                          | 1.56  | 0.24  | 1.63 | 0.24 | 15.5 | 11.6  | 4.71 | 129.5  |    |      |      |      |      |      |       |
| SVS2d                      | 41                   | 69               | 10.1                           | 37.7                           | 9.22  | 2.20 | 7.78 | 1.03              | 5.53             | 1.03                          | 2.80  | 0.40  | 2.50 | 0.32 | 29.8 | 13.9  | 6.26 | 190.6  |    |      |      |      |      |      |       |
| SVS3a                      | 22.8                 | 39.1             | 4.83                           | 17.6                           | 2.90  | 0.97 | 2.11 | 0.26              | 1.35             | 0.23                          | 0.61  | 0.10  | 0.52 | 0.08 | 7.10 | 7.26  | 1.66 | 93.5   |    |      |      |      |      |      |       |
| SVS3b                      | 31.9                 | 48.9             | 7.43                           | 27.7                           | 5.49  | 1.74 | 4.52 | 0.62              | 3.27             | 0.62                          | 1.64  | 0.24  | 1.44 | 0.21 | 17   | 9.95  | 3.23 | 135.7  |    |      |      |      |      |      |       |
| SVS3c                      | 41.1                 | 60.2             | 9.66                           | 37.6                           | 8.70  | 2.63 | 7.89 | 1.14              | 5.96             | 1.15                          | 2.66  | 0.38  | 2.25 | 0.35 | 31.1 | 11.4  | 3.51 | 181.7  |    |      |      |      |      |      |       |
| SVS3d                      | 31.8                 | 54.3             | 7.06                           | 26.9                           | 5.87  | 1.62 | 4.72 | 0.70              | 3.76             | 0.65                          | 1.60  | 0.22  | 1.47 | 0.21 | 19.7 | 10.7  | 7.53 | 140.9  |    |      |      |      |      |      |       |
| ENS1a                      | 49.1                 | 68.8             | 10.4                           | 38.3                           | 8.05  | 1.30 | 7.64 | 1.23              | 7.39             | 1.46                          | 4.42  | 0.62  | 3.81 | 0.59 | 45.2 | 21.1  | 6.27 | 203.1  |    |      |      |      |      |      |       |
| ENS1b                      | 58.5                 | 70               | 14.4                           | 55.3                           | 12.7  | 1.99 | 11.9 | 1.89              | 10.8             | 2.17                          | 5.96  | 0.84  | 5.62 | 0.90 | 60.9 | 20.4  | 5.94 | 252.9  |    |      |      |      |      |      |       |
| ENS1c                      | 54.9                 | 83.8             | 13.6                           | 52                             | 12.6  | 2.04 | 11.9 | 1.90              | 11.2             | 2.10                          | 6.23  | 0.87  | 5.95 | 0.88 | 59.7 | 19.7  | 5.25 | 259.8  |    |      |      |      |      |      |       |
| ENS1d                      | 45.3                 | 99               | 11.5                           | 44.3                           | 11.2  | 1.71 | 10.7 | 1.78              | 10.8             | 2.07                          | 5.77  | 0.82  | 5.58 | 0.84 | 55.6 | 20.5  | 5.27 | 251.2  |    |      |      |      |      |      |       |
| ENS1e                      | 42.3                 | 74.5             | 9.97                           | 37.8                           | 9.12  | 1.41 | 8.85 | 1.37              | 8.19             | 1.66                          | 4.77  | 0.69  | 4.68 | 0.70 | 46.4 | 18.7  | 4.92 | 206.0  |    |      |      |      |      |      |       |
| Stream and beach sediments |                      |                  |                                |                                |       |      |      |                   |                  |                               |       |       |      |      |      |       |      |        |    |      |      |      |      |      |       |
| (ppm)                      |                      | Ce               | Pr                             | Nd                             | Sm    | Eu   | Gd   | Tb                | Dy               | Ho                            | Er    | Tm    | Yb   | Lu   | Y    | Th    | U    | REE    |    |      |      |      |      |      |       |
| SVSS 1                     | 26.2                 | 45.1             | 5.48                           | 19                             | 3.29  | 0.85 | 2.36 | 0.32              | 1.45             | 0.26                          | 0.71  | 0.09  | 0.67 | 0.10 | 7.80 | 6.94  | 1.85 | 105.8  |    |      |      |      |      |      |       |
| SVSS 2                     | 439                  | 799              | 86.9                           | 286                            | 36    | 1.28 | 18.2 | 2.11              | 9.45             | 1.47                          | 3.21  | 0.39  | 2.21 | 0.29 | 36.6 | 110   | 2.96 | 1685.5 |    |      |      |      |      |      |       |
| SVSS 12                    | 23                   | 40.9             | 4.84                           | 16.4                           | 2.57  | 0.66 | 1.83 | 0.24              | 1.32             | 0.25                          | 0.58  | 0.08  | 0.49 | 0.10 | 6.40 | 7.40  | 1.87 | 93.26  |    |      |      |      |      |      |       |
| SVSS 13                    | 1390                 | 2520             | 265                            | 870                            | 99.5  | 1.95 | 39.1 | 3.58              | 12.5             | 1.56                          | 2.78  | 0.30  | 1.59 | 0.21 | 34.5 | 334   | 5.62 | 5208   |    |      |      |      |      |      |       |
| SVSS 14                    | 116                  | 210              | 21.5                           | 69.6                           | 8.08  | 0.40 | 3.19 | 0.35              | 1.51             | 0.18                          | 0.38  | 0.05  | 0.32 | 0.03 | 4.50 | 27.4  | 1.23 | 432    |    |      |      |      |      |      |       |
| SVSS 15                    | >10000               | >10000           | >1000                          | >10000                         | >1000 | 32.9 | 698  | 67.3              | 230              | 27.2                          | 48.80 | 4.92  | 24.3 | 3.21 | 582  | >1000 | 83.7 | >24000 |    |      |      |      |      |      |       |
| SVSS 22                    | 226                  | 386              | 42.9                           | 140                            | 18.3  | 0.62 | 9.36 | 0.98              | 3.86             | 0.58                          | 1.47  | 0.17  | 1.44 | 0.26 | 15.6 | 88.4  | 7.58 | 831    |    |      |      |      |      |      |       |
| ENS 1                      | 7                    | 13.6             | 1.59                           | 5.80                           | 1.21  | 0.11 | 0.94 | 0.17              | 1.16             | 0.23                          | 0.74  | 0.10  | 0.70 | 0.12 | 7    | 4.40  | 1.40 | 33.5   |    |      |      |      |      |      |       |
| ENS 6                      | 9                    | 17.9             | 1.97                           | 7.40                           | 1.74  | 0.21 | 1.62 | 0.22              | 1.55             | 0.35                          | 1.04  | 0.12  | 1.05 | 0.15 | 9.50 | 5.99  | 1.58 | 44.3   |    |      |      |      |      |      |       |

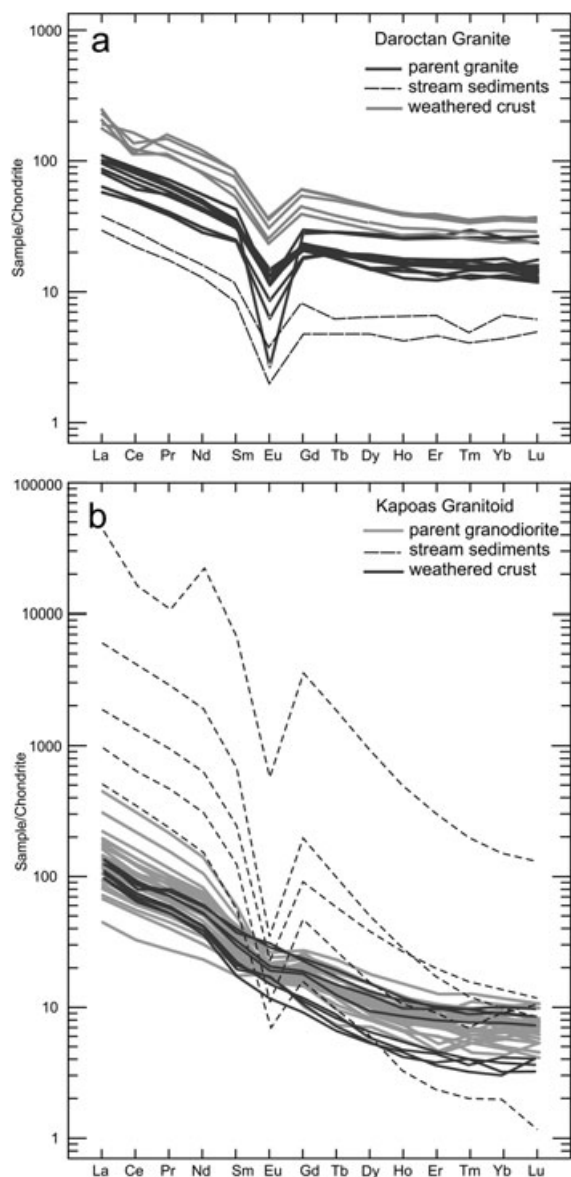


Fig. 8 Spider diagram showing the chondrite-normalized REE pattern of the parent granitic rocks, weathered crust, and stream sediment samples for the (a) Daroetan Granite and the (b) Kapoas Granitoid.

Ce is consistently characterized by a negative anomaly, while Eu, Tm, and Yb vary in the degree of depletion in the ion exchangeable form. The remaining Ce of the weathered crust sample SVS 2d from the Kapoas Granitoid were present as crystalline Fe-oxide occluded (Step 8), organically-bound (Step 6), and amorphous Fe oxide-occluded (Step 7) similar to the weathered crust sample ENS 1 from the Daroetan Granite. However, these were negligible in the

weathered crust sample SVS 2b from the Kapoas Granitoid. Ce behavior in the weathered crust sample SVS 3d from the Kapoas Granitoid is similar with those in the weathered crust samples SVS 2 s from the Kapoas Granitoid and ENS 1 from the Daroetan Granite, wherein it occurs as crystalline Fe-oxide occluded, organically-bound, and amorphous Fe oxide-occluded forms. Similar to ENS 1 samples, Eu and Gd were also present as Mn-oxide occluded (Step 5) and acid soluble (Step 4) forms in the weathered crust samples SVS 3b and 3d from the Kapoas Granitoid.

The LREE extracted from the weathered granitic crusts from the Daroetan Granite and the Kapoas Granitoid are significantly higher than HREE. LREE are dominantly present as ion exchangeable, Pb-displaceable, organically-bound, amorphous Fe oxide-occluded, and crystalline Fe oxide-occluded forms in the weathered crusts of the granitic rocks while HREE is present as acid soluble and Mn oxide-occluded forms in the weathered crusts of the granitic rocks.

## 5. Discussion

Several studies show that the initial concentration of the parent rock, the geographic location, climate condition, annual rainfall, geochemical composition of the parent granite, and geologic age are important parameters for the enrichment of REE to form the ion-adsorption type deposit (Wu *et al.*, 1990; Cocker, 2014; Sanematsu *et al.*, 2015). In this study, a comparison between two plutons with similar geochemical signature but different initial concentrations of REE in the parent granitic rock with different age of magmatism was carried out. The age of ion-adsorption type deposits ranges from 548 Ma to 96 Ma (Cocker, 2014); thus, the Daroetan Granite falls within the criteria for viable sources of ion-adsorption type deposit in terms of age. The ion-adsorption type REE deposits are associated with granites that are metaluminous to weakly peraluminous, with I-type affinity, and are classified into ilmenite series (Sanematsu & Watanabe, 2016). The climate condition and annual rainfall of both units were similar from Middle Miocene (age of magmatism of the Kapoas Granitoid) until the present. However, the initial climate condition and the annual rainfall of the Daroetan Granite was inferred to be different from the present day situation. Since the Daroetan Granite is interpreted to be derived from the southeastern

**Table 3** Result of sequential extraction. REE extracted refers to the percentage of the ion-adsorption type REE in the weathered crust (REE leached / REE in weathered crust \* 100)

| SVS2b                                | La   | Ce   | Pr   | Nd   | Sm   | Eu   | Gd   | Tb   | Dy   | Ho   | Er   | Tm   | Yb   | Lu   | Y     | Th    | U    | REE   | REE extracted |
|--------------------------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|-------|-------|------|-------|---------------|
| <i>Whole rock</i>                    | 32   | 56.3 | 6.57 | 24   | 4.38 | 1.08 | 3.59 | 0.45 | 2.32 | 0.47 | 1.28 | 0.19 | 1.23 | 0.18 | 13.3  | 11.4  | 5.61 | 134.0 |               |
| <i>Exchangeable salts</i>            | 6.20 | 7.40 | 1.57 | 6.60 | 1.70 | 0.39 | 1.61 | 0.23 | 1.20 | 0.23 | 0.53 | 0.05 | 0.35 | 0.05 | 5.42  | 0.00  | 0.00 | 28.1  |               |
| <i>Pb- displaceable</i>              | 0.47 | 0.57 | 0.12 | 0.52 | 0.13 | 0.03 | 0.12 | 0.02 | 0.11 | 0.02 | 0.06 | 0.01 | 0.06 | 0.01 | 0.39  | 0.00  | 0.07 | 2.23  |               |
| <i>Acid soluble</i>                  | 0.01 | 0.02 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01  | 0.12  | 0.18 | 0.06  |               |
| <i>Mn-oxide occluded</i>             | 0.08 | 0.21 | 0.02 | 0.10 | 0.03 | 0.01 | 0.03 | 0.01 | 0.03 | 0.01 | 0.02 | 0.00 | 0.02 | 0.00 | 0.09  | 0.05  | 0.11 | 0.56  |               |
| <i>Organically-bound</i>             | 0.09 | 0.97 | 0.03 | 0.11 | 0.03 | 0.01 | 0.03 | 0.00 | 0.03 | 0.01 | 0.02 | 0.00 | 0.02 | 0.00 | 0.10  | 0.59  | 0.18 | 1.35  |               |
| <i>Amorphous Fe-oxide occluded</i>   | 0.05 | 0.38 | 0.01 | 0.06 | 0.02 | 0.00 | 0.02 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.03  | 0.69  | 0.11 | 0.58  |               |
| <i>Crystalline Fe-oxide occluded</i> | 1.13 | 2.07 | 0.11 | 0.41 | 0.10 | 0.02 | 0.09 | 0.01 | 0.09 | 0.02 | 0.05 | 0.01 | 0.06 | 0.01 | 0.25  | 1.56  | 1.01 | 4.19  |               |
| Total leached (Step 2 to 8)          | 8.02 | 11.6 | 1.87 | 7.80 | 2.00 | 0.46 | 1.90 | 0.28 | 1.49 | 0.28 | 0.69 | 0.08 | 0.52 | 0.07 | 6.29  | 3     | 1.66 | 37.1  | 29.4          |
| SVS2d                                |      |      |      |      |      |      |      |      |      |      |      |      |      |      |       |       |      |       |               |
| <i>Whole rock</i>                    | 41   | 69   | 10.1 | 37.7 | 9.22 | 2.20 | 7.78 | 1.03 | 5.53 | 1.03 | 2.80 | 0.40 | 2.50 | 0.32 | 29.80 | 13.85 | 6.26 | 190.6 |               |
| <i>Exchangeable salts</i>            | 7.34 | 4.27 | 2.06 | 8.93 | 2.37 | 0.64 | 2.29 | 0.34 | 1.84 | 0.32 | 0.84 | 0.09 | 0.63 | 0.10 | 7.85  | 0.00  | 0.01 | 32.1  |               |
| <i>Pb- displaceable</i>              | 0.78 | 0.63 | 0.28 | 1.21 | 0.38 | 0.10 | 0.36 | 0.06 | 0.33 | 0.06 | 0.17 | 0.02 | 0.16 | 0.02 | 1.07  | 0.00  | 0.19 | 4.57  |               |
| <i>Acid soluble</i>                  | 0.03 | 0.05 | 0.01 | 0.05 | 0.02 | 0.01 | 0.02 | 0.00 | 0.02 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.05  | 0.11  | 0.29 | 0.24  |               |
| <i>Mn-oxide occluded</i>             | 0.17 | 0.46 | 0.07 | 0.30 | 0.10 | 0.03 | 0.11 | 0.02 | 0.11 | 0.02 | 0.05 | 0.01 | 0.05 | 0.01 | 0.31  | 0.04  | 0.11 | 1.50  |               |
| <i>Organically-bound</i>             | 0.52 | 4.47 | 0.17 | 0.75 | 0.21 | 0.05 | 0.23 | 0.03 | 0.18 | 0.04 | 0.11 | 0.02 | 0.11 | 0.02 | 0.76  | 1.78  | 0.18 | 6.91  |               |
| <i>Amorphous Fe-oxide occluded</i>   | 0.16 | 2.08 | 0.06 | 0.28 | 0.09 | 0.03 | 0.10 | 0.01 | 0.07 | 0.01 | 0.02 | 0.00 | 0.02 | 0.00 | 0.14  | 0.63  | 0.06 | 2.94  |               |
| <i>Crystalline Fe-oxide occluded</i> | 0.84 | 4.44 | 0.27 | 1.13 | 0.31 | 0.07 | 0.32 | 0.04 | 0.23 | 0.04 | 0.12 | 0.02 | 0.11 | 0.02 | 0.77  | 1.12  | 0.52 | 7.95  |               |
| Total leached (Step 2 to 8)          | 9.83 | 16.4 | 2.92 | 12.7 | 3.48 | 0.93 | 3.43 | 0.50 | 2.78 | 0.49 | 1.33 | 0.16 | 1.10 | 0.16 | 10.95 | 3.69  | 1.36 | 56.2  | 30.5          |
| SVS3a                                |      |      |      |      |      |      |      |      |      |      |      |      |      |      |       |       |      |       |               |
| <i>Whole rock</i>                    | 22.8 | 39.1 | 4.83 | 17.6 | 2.90 | 0.97 | 2.11 | 0.26 | 1.35 | 0.23 | 0.61 | 0.10 | 0.52 | 0.08 | 7.10  | 7.26  | 1.66 | 93.5  |               |
| <i>Exchangeable salts</i>            | 2.72 | 2.84 | 0.71 | 2.90 | 0.66 | 0.24 | 0.61 | 0.11 | 0.61 | 0.11 | 0.27 | 0.03 | 0.22 | 0.02 | 2.42  | 0.00  | 0.01 | 12.1  |               |
| <i>Pb- displaceable</i>              | 0.18 | 0.21 | 0.05 | 0.22 | 0.07 | 0.02 | 0.06 | 0.01 | 0.06 | 0.01 | 0.03 | 0.00 | 0.03 | 0.00 | 0.18  | 0.00  | 0.09 | 0.96  |               |
| <i>Acid soluble</i>                  | 0.01 | 0.03 | 0.01 | 0.03 | 0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02  | 0.14  | 0.13 | 0.11  |               |
| <i>Mn-oxide occluded</i>             | 0.04 | 0.14 | 0.01 | 0.06 | 0.02 | 0.01 | 0.02 | 0.00 | 0.02 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.05  | 0.02  | 0.06 | 0.34  |               |
| <i>Organically-bound</i>             | 0.10 | 1.27 | 0.03 | 0.15 | 0.04 | 0.01 | 0.04 | 0.01 | 0.04 | 0.01 | 0.02 | 0.00 | 0.02 | 0.00 | 0.14  | 0.74  | 0.18 | 1.75  |               |
| <i>Amorphous Fe-oxide occluded</i>   | 0.05 | 0.64 | 0.02 | 0.09 | 0.03 | 0.01 | 0.03 | 0.00 | 0.02 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.04  | 0.41  | 0.04 | 0.90  |               |
| <i>Crystalline Fe-oxide occluded</i> | 1    | 3.05 | 0.32 | 1.42 | 0.39 | 0.11 | 0.38 | 0.05 | 0.27 | 0.05 | 0.13 | 0.02 | 0.10 | 0.02 | 0.88  | 0.95  | 0.28 | 7.29  |               |
| Total leached (Step 2 to 8)          | 4.10 | 8.18 | 1.15 | 4.86 | 1.22 | 0.40 | 1.16 | 0.19 | 1.01 | 0.19 | 0.47 | 0.05 | 0.40 | 0.05 | 3.73  | 2.27  | 0.79 | 23.4  | 27            |
| SVS3b                                |      |      |      |      |      |      |      |      |      |      |      |      |      |      |       |       |      |       |               |
| <i>Whole rock</i>                    | 31.9 | 48.9 | 7.43 | 27.7 | 5.49 | 1.74 | 4.52 | 0.62 | 3.27 | 0.62 | 1.64 | 0.24 | 1.44 | 0.21 | 17    | -     | -    | 135.7 |               |
| <i>Exchangeable salts</i>            | 2.87 | 1.54 | 0.81 | 3.43 | 0.92 | 0.33 | 0.85 | 0.13 | 0.70 | 0.13 | 0.38 | 0.05 | 0.35 | 0.05 | 3.29  | -     | -    | 12.6  |               |
| <i>Pb- displaceable</i>              | 0.15 | 0.11 | 0.06 | 0.26 | 0.09 | 0.03 | 0.08 | 0.01 | 0.08 | 0.02 | 0.05 | 0.01 | 0.05 | 0.01 | 0.23  | -     | -    | 1     |               |
| <i>Acid soluble</i>                  | 0.00 | 0.00 | 0.00 | 0.01 | 0.03 | 0.31 | 0.37 | 0.02 | 0.02 | 0.00 | 0.04 | 0.00 | 0.05 | 0.00 | 0.00  | -     | -    | 0.87  |               |
| <i>Mn-oxide occluded</i>             | 0.01 | 0.04 | 0.00 | 0.03 | 0.03 | 0.20 | 0.37 | 0.03 | 0.03 | 0.01 | 0.05 | 0.00 | 0.06 | 0.01 | 0.02  | -     | -    | 0.87  |               |
| <i>Organically-bound</i>             | 0.04 | 0.50 | 0.01 | 0.06 | 0.03 | 0.02 | 0.17 | 0.01 | 0.02 | 0.00 | 0.02 | 0.00 | 0.02 | 0.00 | 0.07  | -     | -    | 16.0  |               |
| <i>Amorphous Fe-oxide occluded</i>   | 0.04 | 0.78 | 0.02 | 0.08 | 0.03 | 0.01 | 0.03 | 0.00 | 0.02 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.05  | -     | -    | 1.01  |               |
| <i>Crystalline Fe-oxide occluded</i> | 1.08 | 2.27 | 0.35 | 1.65 | 0.45 | 0.14 | 0.41 | 0.06 | 0.29 | 0.05 | 0.15 | 0.02 | 0.13 | 0.02 | 1.31  | -     | -    | 7.05  |               |
| Total leached (Step 2 to 8)          | 4.20 | 5.24 | 1.25 | 5.52 | 1.57 | 1.05 | 2.28 | 0.26 | 1.14 | 0.22 | 0.69 | 0.09 | 0.68 | 0.09 | 4.97  | -     | -    | 24.3  | 19.2          |
| SVS3d                                |      |      |      |      |      |      |      |      |      |      |      |      |      |      |       |       |      |       |               |
| <i>Whole rock</i>                    | 31.8 | 54.3 | 7.06 | 26.0 | 5.87 | 1.62 | 4.72 | 0.70 | 3.76 | 0.65 | 1.60 | 0.22 | 1.47 | 0.21 | 19.70 | -     | -    | 140.9 |               |

Table 3. (Continued)

| SVS2b                                | La   | Ce    | Pr    | Nd    | Sm    | Eu   | Gd    | Tb   | Dy    | Ho   | Er   | Tm   | Yb   | Lu   | Y     | Th   | U    | REE    | REE<br>extracted |
|--------------------------------------|------|-------|-------|-------|-------|------|-------|------|-------|------|------|------|------|------|-------|------|------|--------|------------------|
| <i>Exchangeable salts</i>            | 8.53 | 3.62  | 2     | 7.82  | 1.79  | 0.60 | 1.85  | 0.27 | 1.45  | 0.27 | 0.73 | 0.09 | 0.51 | 0.07 | 8.20  | -    | -    | 29.6   |                  |
| <i>Pb- displaceable</i>              | 0.38 | 0.00  | 0.14  | 0.63  | 0.18  | 0.08 | 0.17  | 0.03 | 0.18  | 0.03 | 0.09 | 0.01 | 0.09 | 0.01 | 0.63  | -    | -    | 2.03   |                  |
| <i>Acid soluble</i>                  | 0.01 | 0.01  | 0.00  | 0.02  | 0.03  | 0.25 | 0.62  | 0.04 | 0.04  | 0.01 | 0.07 | 0.01 | 0.10 | 0.01 | 0.01  | -    | -    | 1.22   |                  |
| <i>Mn-oxide occluded</i>             | 0.03 | 0.16  | 0.01  | 0.07  | 0.06  | 0.10 | 0.84  | 0.06 | 0.07  | 0.01 | 0.11 | 0.01 | 0.13 | 0.01 | 0.07  | -    | -    | 1.69   |                  |
| <i>Organically-bound</i>             | 0.16 | 3.70  | 0.06  | 0.24  | 0.07  | 0.02 | 0.09  | 0.01 | 0.07  | 0.01 | 0.04 | 0.01 | 0.05 | 0.01 | 0.26  | -    | -    | 4.55   |                  |
| <i>Amorphous Fe-oxide occluded</i>   | 0.09 | 2.78  | 0.03  | 0.15  | 0.05  | 0.02 | 0.06  | 0.01 | 0.04  | 0.01 | 0.01 | 0.00 | 0.01 | 0.00 | 0.09  | -    | -    | 3.25   |                  |
| <i>Crystalline Fe-oxide occluded</i> | 1.74 | 4.99  | 0.52  | 2.23  | 0.52  | 0.17 | 0.49  | 0.06 | 0.30  | 0.06 | 0.15 | 0.02 | 0.11 | 0.02 | 1.49  | -    | -    | 11.4   |                  |
| <i>Total leached (Step 2 to 8)</i>   | 10.9 | 15.3  | 2.78  | 11.2  | 2.71  | 1.24 | 4.12  | 0.49 | 2.16  | 0.40 | 1.22 | 0.15 | 1.00 | 0.13 | 10.8  | -    | -    | 53.7   | 40.2             |
| ENS1a                                |      |       |       |       |       |      |       |      |       |      |      |      |      |      |       |      |      |        |                  |
| <i>Whole rock</i>                    | 49.1 | 68.8  | 10.4  | 38.3  | 8.05  | 1.30 | 7.64  | 1.23 | 7.39  | 1.46 | 4.42 | 0.62 | 3.81 | 0.59 | 45.2  | 21.1 | 6.27 | 203.1  |                  |
| <i>Exchangeable salts</i>            | 24.1 | 16.3  | 5.21  | 19.8  | 3.69  | 0.55 | 3.75  | 0.58 | 3.57  | 0.70 | 1.94 | 0.25 | 1.47 | 0.20 | 18.7  | 0.00 | 0.00 | 82.1   |                  |
| <i>Pb- displaceable</i>              | 1.85 | 1.86  | 0.56  | 2.15  | 0.54  | 0.09 | 0.51  | 0.09 | 0.57  | 0.11 | 0.33 | 0.05 | 0.34 | 0.05 | 2.08  | 0.00 | 0.07 | 9.08   |                  |
| <i>Acid soluble</i>                  | 0.07 | 0.23  | 0.03  | 0.13  | 0.04  | 0.01 | 0.04  | 0.01 | 0.04  | 0.01 | 0.03 | 0.00 | 0.03 | 0.00 | 0.12  | 0.06 | 0.20 | 0.68   |                  |
| <i>Mn-oxide occluded</i>             | 0.20 | 1.13  | 0.07  | 0.27  | 0.08  | 0.01 | 0.08  | 0.02 | 0.10  | 0.02 | 0.06 | 0.01 | 0.08 | 0.01 | 0.28  | 0.02 | 0.18 | 2.14   |                  |
| <i>Organically-bound</i>             | 0.27 | 3.69  | 0.09  | 0.34  | 0.09  | 0.01 | 0.10  | 0.02 | 0.11  | 0.03 | 0.10 | 0.02 | 0.15 | 0.02 | 0.45  | 2.92 | 0.43 | 5.02   |                  |
| <i>Amorphous Fe-oxide occluded</i>   | 0.22 | 3.18  | 0.08  | 0.34  | 0.09  | 0.02 | 0.11  | 0.02 | 0.10  | 0.02 | 0.05 | 0.01 | 0.04 | 0.00 | 0.19  | 1.25 | 0.07 | 4.27   |                  |
| <i>Crystalline Fe-oxide occluded</i> | 0.70 | 8.50  | 0.23  | 0.89  | 0.22  | 0.04 | 0.25  | 0.04 | 0.24  | 0.05 | 0.15 | 0.02 | 0.18 | 0.03 | 0.66  | 3.32 | 0.55 | 11.5   | 55.3             |
| <i>Total leached (Step 2 to 8)</i>   | 27.4 | 34.9  | 6.26  | 23.9  | 4.75  | 0.72 | 4.83  | 0.76 | 4.74  | 0.93 | 2.66 | 0.36 | 2.28 | 0.32 | 22.5  | 7.56 | 1.51 | 114.8  |                  |
| ENS1b                                |      |       |       |       |       |      |       |      |       |      |      |      |      |      |       |      |      |        |                  |
| <i>Whole rock</i>                    | 58.5 | 70.00 | 14.40 | 55.30 | 12.65 | 1.99 | 11.95 | 1.89 | 10.75 | 2.17 | 5.96 | 0.84 | 5.62 | 0.90 | 60.90 | -    | -    | 252.92 |                  |
| <i>Exchangeable salts</i>            | 37.4 | 10.4  | 9.79  | 37.5  | 8.24  | 1.38 | 8.14  | 1.26 | 7.05  | 1.43 | 3.94 | 0.54 | 3.33 | 0.49 | 38.6  | -    | -    | 130.8  |                  |
| <i>Pb- displaceable</i>              | 1.74 | 0.57  | 0.61  | 2.43  | 0.67  | 0.12 | 0.61  | 0.12 | 0.73  | 0.14 | 0.42 | 0.07 | 0.48 | 0.07 | 2.79  | -    | -    | 8.77   |                  |
| <i>Acid soluble</i>                  | 0.01 | 0.01  | 0.00  | 0.02  | 0.04  | 0.11 | 0.87  | 0.06 | 0.05  | 0.01 | 0.11 | 0.01 | 0.18 | 0.01 | 0.02  | -    | -    | 1.50   |                  |
| <i>Mn-oxide occluded</i>             | 0.06 | 0.23  | 0.03  | 0.15  | 0.10  | 0.09 | 1.24  | 0.08 | 0.13  | 0.03 | 0.18 | 0.02 | 0.27 | 0.03 | 0.17  | -    | -    | 2.66   |                  |
| <i>Organically-bound</i>             | 0.25 | 6.24  | 0.11  | 0.43  | 0.13  | 0.03 | 0.15  | 0.02 | 0.17  | 0.04 | 0.14 | 0.03 | 0.22 | 0.03 | 0.57  | -    | -    | 7.98   |                  |
| <i>Amorphous Fe-oxide occluded</i>   | 0.23 | 4.77  | 0.10  | 0.41  | 0.14  | 0.02 | 0.15  | 0.02 | 0.15  | 0.02 | 0.06 | 0.01 | 0.06 | 0.01 | 0.27  | -    | -    | 6.14   |                  |
| <i>Crystalline Fe-oxide occluded</i> | 0.50 | 9.95  | 0.19  | 0.77  | 0.23  | 0.05 | 0.26  | 0.04 | 0.26  | 0.05 | 0.17 | 0.03 | 0.22 | 0.03 | 0.74  | -    | -    | 12.75  |                  |
| <i>Total leached (Step 2 to 8)</i>   | 40.1 | 32.2  | 10.8  | 41.7  | 9.53  | 1.80 | 11.4  | 1.61 | 8.55  | 1.71 | 5.04 | 0.69 | 4.76 | 0.67 | 43.17 | -    | -    | 170.6  | 68.1             |
| ENS1c                                |      |       |       |       |       |      |       |      |       |      |      |      |      |      |       |      |      |        |                  |
| <i>Whole rock</i>                    | 54.9 | 83.8  | 13.6  | 52    | 12.6  | 2.04 | 11.9  | 1.90 | 11.20 | 2.10 | 6.23 | 0.87 | 5.95 | 0.88 | 59.7  | -    | -    | 259.8  |                  |
| <i>Exchangeable salts</i>            | 38.7 | 5.49  | 10.1  | 39.2  | 9     | 1.50 | 8.54  | 1.33 | 7.50  | 1.45 | 4.14 | 0.53 | 3.42 | 0.50 | 38.9  | -    | -    | 131.4  |                  |
| <i>Pb- displaceable</i>              | 1.69 | 0.19  | 0.59  | 2.33  | 0.67  | 0.12 | 0.61  | 0.12 | 0.76  | 0.14 | 0.44 | 0.07 | 0.53 | 0.07 | 2.76  | -    | -    | 8.34   |                  |
| <i>Acid soluble</i>                  | 0.01 | 0.01  | 0.00  | 0.03  | 0.04  | 0.28 | 0.61  | 0.04 | 0.05  | 0.01 | 0.08 | 0.01 | 0.14 | 0.01 | 0.02  | -    | -    | 1.31   |                  |
| <i>Mn-oxide occluded</i>             | 0.06 | 0.30  | 0.03  | 0.14  | 0.09  | 0.12 | 0.92  | 0.06 | 0.12  | 0.02 | 0.14 | 0.02 | 0.22 | 0.02 | 0.18  | -    | -    | 2.27   |                  |
| <i>Organically-bound</i>             | 0.22 | 10.6  | 0.10  | 0.37  | 0.12  | 0.03 | 0.17  | 0.02 | 0.16  | 0.03 | 0.12 | 0.02 | 0.20 | 0.03 | 0.47  | -    | -    | 12.2   |                  |
| <i>Amorphous Fe-oxide occluded</i>   | 0.16 | 6.52  | 0.07  | 0.30  | 0.11  | 0.02 | 0.13  | 0.02 | 0.13  | 0.02 | 0.06 | 0.01 | 0.06 | 0.01 | 0.22  | -    | -    | 7.60   |                  |
| <i>Crystalline Fe-oxide occluded</i> | 0.47 | 25.6  | 0.18  | 0.68  | 0.22  | 0.05 | 0.36  | 0.05 | 0.31  | 0.06 | 0.19 | 0.03 | 0.28 | 0.04 | 0.81  | -    | -    | 28.5   |                  |
| <i>Total leached (Step 2 to 8)</i>   | 41.3 | 48.7  | 11.1  | 43.0  | 10.2  | 2.11 | 11.3  | 1.64 | 9.03  | 1.75 | 5.18 | 0.69 | 4.84 | 0.68 | 43.3  | -    | -    | 191.6  | 73.5             |
| ENS1d                                |      |       |       |       |       |      |       |      |       |      |      |      |      |      |       |      |      |        |                  |
| <i>Whole rock</i>                    | 45.3 | 99    | 11.5  | 44.3  | 11.2  | 1.71 | 10.7  | 1.78 | 10.6  | 2.07 | 5.77 | 0.82 | 5.58 | 0.84 | 55.6  | 20.5 | 5.27 | 251.2  |                  |
| <i>Exchangeable salts</i>            | 21.5 | 8.76  | 5.69  | 22.2  | 5.08  | 0.79 | 4.97  | 0.80 | 4.64  | 0.89 | 2.41 | 0.32 | 2.02 | 0.28 | 19.8  | 0.00 | 0.00 | 80.3   |                  |

Table 3. (Continued)

| SVS2b                         | La   | Ce   | Pr   | Nd    | Sm   | Eu   | Gd   | Tb   | Dy   | Ho   | Er   | Tm   | Yb   | Lu   | Y    | Th   | U    | REE   | REE extracted |
|-------------------------------|------|------|------|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|-------|---------------|
| Pb-displaceable               | 1.82 | 1.23 | 0.63 | 2.50  | 0.70 | 0.12 | 0.66 | 0.12 | 0.75 | 0.14 | 0.42 | 0.06 | 0.46 | 0.06 | 2.37 | 0.00 | 0.05 | 9.67  |               |
| Acid soluble                  | 0.09 | 0.17 | 0.04 | 0.19  | 0.07 | 0.01 | 0.06 | 0.01 | 0.07 | 0.01 | 0.04 | 0.01 | 0.06 | 0.01 | 0.18 | 0.26 | 0.18 | 0.85  |               |
| Mn-oxide occluded             | 0.23 | 0.79 | 0.09 | 0.36  | 0.11 | 0.02 | 0.11 | 0.02 | 0.14 | 0.03 | 0.09 | 0.01 | 0.12 | 0.02 | 0.37 | 0.04 | 0.13 | 2.14  |               |
| Organically-bound             | 0.33 | 14.6 | 0.13 | 0.49  | 0.14 | 0.02 | 0.22 | 0.03 | 0.17 | 0.04 | 0.12 | 0.02 | 0.17 | 0.03 | 0.55 | 2.27 | 0.35 | 16.5  |               |
| Amorphous Fe-oxide occluded   | 0.17 | 7.48 | 0.07 | 0.29  | 0.10 | 0.02 | 0.13 | 0.02 | 0.11 | 0.02 | 0.05 | 0.01 | 0.05 | 0.01 | 0.17 | 1.42 | 0.10 | 8.53  |               |
| Crystalline Fe-oxide occluded | 0.79 | 17.2 | 0.23 | 0.91  | 0.29 | 0.05 | 0.35 | 0.06 | 0.39 | 0.08 | 0.25 | 0.04 | 0.32 | 0.04 | 0.91 | 4.80 | 0.73 | 20.97 |               |
| Total leached (Step 2 to 8)   | 24.9 | 50.2 | 6.88 | 26.9  | 6.47 | 1.03 | 6.49 | 1.05 | 6.28 | 1.20 | 3.39 | 0.48 | 3.20 | 0.45 | 24.4 | 8.80 | 1.55 | 138.9 | 53.3          |
| ENSle                         |      |      |      |       |      |      |      |      |      |      |      |      |      |      |      |      |      |       |               |
| Whole rock                    | 42.3 | 74.5 | 9.97 | 37.8  | 9.12 | 1.41 | 8.85 | 1.37 | 8.19 | 1.66 | 4.77 | 0.69 | 4.68 | 0.70 | 46.4 | -    | -    | 206   |               |
| Exchangeable salts            | 25.4 | 3.37 | 6.32 | 23.8  | 5.11 | 0.89 | 4.94 | 0.77 | 4.44 | 0.89 | 2.53 | 0.33 | 2.04 | 0.28 | 23.7 | -    | -    | 81.1  |               |
| Pb-displaceable               | 1.03 | 0.07 | 0.34 | 1.34  | 0.36 | 0.07 | 0.32 | 0.06 | 0.41 | 0.08 | 0.24 | 0.04 | 0.28 | 0.04 | 1.58 | -    | -    | 4.67  |               |
| Acid soluble                  | 0.01 | 0.01 | 0.00 | 0.02  | 0.02 | 0.10 | 0.35 | 0.02 | 0.03 | 0.01 | 0.05 | 0.00 | 0.06 | 0.01 | 0.02 | -    | -    | 0.69  |               |
| Mn-oxide occluded             | 0.09 | 0.59 | 0.03 | 0.16  | 0.09 | 0.40 | 0.82 | 0.05 | 0.10 | 0.02 | 0.12 | 0.01 | 0.16 | 0.02 | 0.19 | -    | -    | 2.66  |               |
| Organically-bound             | 0.15 | 13.2 | 0.06 | 0.21  | 0.06 | 0.02 | 0.13 | 0.01 | 0.09 | 0.02 | 0.07 | 0.01 | 0.11 | 0.01 | 0.25 | -    | -    | 14.1  |               |
| Amorphous Fe-oxide occluded   | 0.13 | 6.68 | 0.05 | 0.19  | 0.06 | 0.01 | 0.09 | 0.01 | 0.08 | 0.01 | 0.04 | 0.01 | 0.04 | 0.01 | 0.14 | -    | -    | 7.41  |               |
| Crystalline Fe-oxide occluded | 0.42 | 12.6 | 0.14 | 0.52  | 0.15 | 0.03 | 0.22 | 0.03 | 0.23 | 0.05 | 0.15 | 0.02 | 0.19 | 0.03 | 0.69 | -    | -    | 14.8  |               |
| Total leached (Step 2 to 8)   | 27.3 | 36.5 | 6.94 | 26.24 | 5.84 | 1.52 | 6.87 | 0.96 | 5.37 | 1.07 | 3.18 | 0.43 | 2.88 | 0.39 | 26.6 | -    | -    | 125.4 | 60.2          |

Eurasian margin, the climate condition and rainfall amount is similar to that of the eastern China margin during the Cretaceous. Although the exact location of PCB during that time is still debatable, the paleomagnetic work of Almasco *et al.* (2000) resulted in an average of 25.5°N latitude for the Guinlo Formation and Busuanga Chert (Liminangcong Formation). In the present conditions, the favorable geographic location, whose latitude less than 30° N (Cocker, 2014), was also satisfied since the latitude of the study areas are currently located less than 12° N. The western part of Palawan Island, including the study areas, experience dry climate from November to April and wet during the rest of the year. Mean annual rainfall reported for the central Palawan ranges from 1600 to 3000 mm (Baillie *et al.*, 2000).

In the weathered crusts of granitic rocks in northern Palawan, only the samples from Daroetan Granite were collected from the complete profile of weathered crusts as defined by Wu *et al.* (1990), which consist of the surface zone, wholly weathered zone, and sub-weathered zone. The examined profile of the weathered crust of the Kapoas Granitoid lack surface zone and only consist of the wholly weathered zone and sub-weathered zone. In the samples of the weathered crust of the Daroetan Granite with the surface zone, montmorillonite is present. The samples SVS 2 from the upper part of the weathered crust of granitic rocks also contain montmorillonite despite being part of the wholly weathered zone. It may have been part of the transition between the two horizons, the surface zone and the wholly weathered zone. Analysis of the chemical composition of minerals using SEM-EDS shows that the REE-bearing minerals are monazite and xenotime in the weathered crusts of the Daroetan Granite and only monazite in the weathered crusts of the Kapoas Granitoid. Goethite and Fe-rich chlorite formed at the edges of biotite grains in the Kapoas Granitoid sample. In both samples, biotite is altered into vermiculite. Secondary REE-bearing minerals, such as cerianite, were observed in the weathered crust of the Daroetan Granite but not recognized in the weathered crust of the Kapoas Granitoid. The different stages of vermiculite alteration can be gleaned on the samples of weathered crusts from these two units. Weathering of biotite can result in interstratified clay minerals to vermiculite and smectite, then alter to kaolinite (Fordham, 1990). In the sample from weathered crust of the Kapoas Granitoid, vermiculite is not significantly altered while in the weathered crust sample of the Daroetan Granite, differences in the bright and

dark bands in the BSE images reflect difference in the composition as shown by the elements identified in the EDS spectra diagrams, which suggest alteration of vermiculite. The initial stage is the loss of K, followed by the increase in Al and Si content, and an addition of P and Cl. Later stage alteration accompanies enrichment of metals such as Pb and Ba. Formation of cerianite was also associated with the formation of Fe and Mn oxides.

The CIA of representative samples from weathered crust shows that both the Daroctan Granite and Kapoas Granitoid are already in the advanced weathering trend that is delineated by kaolinite minerals. As in most weathering products, the  $\text{SiO}_2$  content is depleted, and  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  are enriched (e.g. Morteani & Preinfalk, 1996).  $\text{P}_2\text{O}_5$ , CaO,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  also tend to commonly decrease (e.g. Wu *et al.*, 1990; Morteani & Preinfalk, 1996). REE are enriched in weathered crusts of the Daroctan Granite while REE are depleted in the stream sediments. On the other hand, REE are depleted in the weathered crust of the Kapoas Granitoid compared to the parent granite, while REE are enriched in the stream and beach sediments. The Kapoas Granitoid shows potential for placer-type deposit. Moreover, despite the relatively higher initial REE content of the Kapoas Granitoid parent rock (53 to 243 ppm) compared to the Daroctan Granite (80 to 143 ppm), REE are enriched in the weathered crust in the Daroctan Granite significantly. Bao and Zhao (2008) reported that the LREE and HREE contents of the LREE-enriched parent granites in South China are approximately 217 to 723 ppm and 25 to 39 ppm, respectively while the LREE and HREE contents of the HREE-enriched parent granites are about 80 ppm and 78 ppm, respectively. The LREE content of parent granitic rocks of the Kapoas Granitoid ranges from 46 to 220 ppm and HREE from 6 to 23 ppm, straddle within the criteria for the LREE-enrichment at the lower limit. The LREE and HREE contents of parent granitic rocks of the Daroctan Granite, on the other hand, range from 64 to 118 ppm and 14 to 25 ppm, respectively and do not fall within the range of the LREE-enriched parent granite. This shows that the initial REE concentration of the parent rock is a less important criterion in prospecting for ion-adsorption type REE deposit as exemplified by the placer-type of deposit associated with the Kapoas Granitoid and the potential ion-adsorption type deposit for the Daroctan Granite.

Negative Ce anomalies are displayed in the weathered crusts of the Daroctan Granite and Kapoas

Granitoid samples in all horizons except for the sample ENS 1d, which is part of the sub-weathered zone (horizon C) of the Daroctan Granite. Sanematsu *et al.* (2013) showed that horizons with positive Ce anomaly and negative Ce anomaly correspond to the top and bottom layer, respectively. The horizons with positive Ce anomaly correspond to the leaching zone where the  $\text{REE}^{3+}$  (except Ce) were leached, transported, and eventually accumulated in the bottom horizons, which are called the accumulation zone (Sanematsu & Watanabe, 2016). The horizon with positive Ce anomaly is an oxidized zone wherein  $\text{Ce}^{3+}$  was oxidized to  $\text{Ce}^{4+}$  in an acidic soil water (Sanematsu *et al.*, 2013; Sanematsu & Watanabe, 2016). The  $\text{Ce}^{4+}$  was fixed as cerianite associated with Fe and Mn-oxide as shown in the weathered crust ENS 1d of the Daroctan Granite. The increased  $\text{Fe}_2\text{O}_3$  content of the weathered granitic crusts from the Daroctan Granite compared to the parent granite shows the influence of Fe-oxides on Ce. This association was observed in the ENS 1c sample wherein cerianite occur together with Fe and Mn oxides. The sequential leaching experimental results show that 21 to 58 % and 34 to 66 % of Ce adheres to the Fe-oxides of the weathered crust of the Kapoas Granitoid and Daroctan Granite, respectively. The profiles of Ce anomaly, REE contents, and REE adsorbed in the weathered horizon (Fig. 9) show an inverse

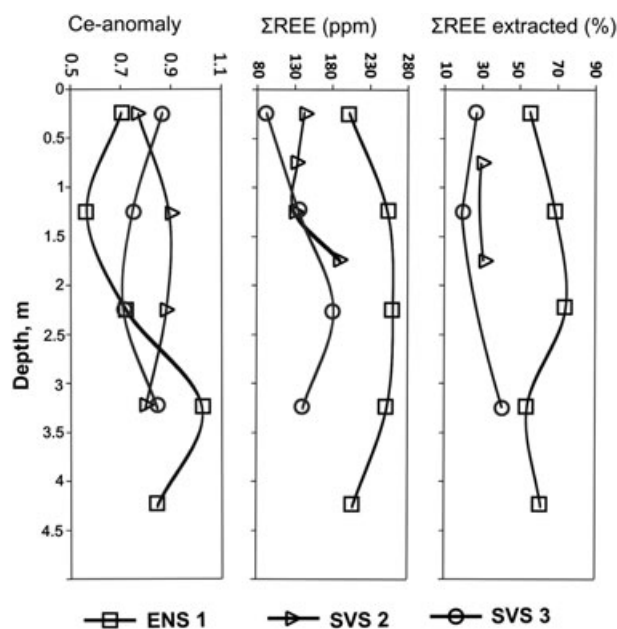


Fig. 9 Depth versus Ce anomaly, REE, and REE extracted from the weathered crust samples of the Daroctan Granite sample and Kapoas Granitoid.

relationship among Ce anomaly and REE contents in the outcrop SVS 2 and SVS 3 from the Kapoas Granitoid. Ce anomaly and adsorbed REE also show an inverse relationship in the outcrop ENS 1 from the Daroctan Granite.

Sequential leaching extraction did not yield a high proportion of REE extracted in the weathered crust of Kapoas Granitoid, which suggests that the REE did not occur as an ion-adsorption state but remained in the refractory phases such as monazite and allanite. Daroctan, on the other hand, is a potential ion-adsorption type LREE source as a significant fraction of REE (about 53 to 74 % of the REE leached fraction) were effectively leached using reagents. As observed in the SEM-EDS, cerianite occurs with Fe and Mn oxides, from where Ce was removed using an oxalate reagent ( $\text{H}_2\text{C}_2\text{O}_4$ ) for REE occluded in Fe-oxide.

In general, REE can occur in different phases in a weathered crust such as trace components in residual minerals, as secondary REE phases such as cerianite, as trace components of Fe and Mn oxides, and as exchangeable cations on clays (Cocker, 2014). In the weathered profiles in Thailand (Imai *et al.*, 2012; Sanematsu *et al.*, 2013) the ion exchangeable fractions are mostly adsorbed on kaolinite.

## 6. Conclusions

The ilmenite series, high-K calc-alkaline, I- and S-type granite type Daroctan Granite and Kapoas Granitoid show mostly similar mineralogical and geochemical signatures. The initial REE content of the parent granite is a less important criterion in ion-adsorption type REE deposit as exemplified by the Kapoas Granitoid and the Daroctan Granite. In both plutons, the residual REE-bearing minerals are mostly monazite. Allanite is only present in the Kapoas Granitoid while the Daroctan Granite contains xenotime. The elevated LREE concentration of stream sediments and beach sands (containing La, Ce, Nd and Sm up to >10,000 ppm) in the areas overlain by the Kapoas Granitoid shows its potential for placer-type deposit containing monazite and allanite. The important parameters in the enrichment of REE in the weathered crust of granitic rocks are the formation of secondary REE-bearing minerals and adsorption of REE on the surface of clay minerals such as vermiculite. Salt solution effectively leached most of the fractions of REE adsorbed on clay minerals.

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