Geochemical anatomy of a spheroidally weathered diabase

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ABSTRACT

Major, trace element concentrations and Nd, Sr isotope ratios were measured in micro-drilled samples of a 2.37 Ga-old, hand-specimen sized spheroidally weathered diabase from southern India. A sample of the un-weathered diabase dike was also analyzed. X-ray micro-CT imaging of the weathered sample shows three dominant mineral phases which are plagioclase, pyroxene, and a Fe-bearing phase (possibly hematite and/or ilmenite). This imaging documents the pervasive nature of two generations of ribbon-like, cross-cutting fractures. The older fracture is sealed while the more recent fracture is open without any in-filling. The values of the Chemical Index of Alteration (CIA) of the samples show a wide range but are less than 50. Despite being a relatively less weathered rock, we observe that concentrations of major, minor and trace elements vary significantly with the percentage relative standard deviation (%RSD) for the elements ranging from 10.2–41.8. The CIA of the samples do not show any trend with the position of the sample in the hand-specimen. Barring Ca and Li, whose concentrations decrease from the core to the rim of the sample, there is no significant spatial trend in the concentrations of the elements.

Concentrations of Na, Al, and Sr increase with increasing CIA values while concentrations of Mg, Fe, and Sc decrease with increasing CIA. The strong positive correlations of Na and Al, as well as Na and Sr indicates preferential weathering of plagioclase in the diabase. Na/Ca increases while Mg/Al, Mg/Na, Mg/Ca, Fe/Al and Sc/Sr decrease with increasing CIA values and the un-weathered rock plots in the middle of these trends. Such variations are explained in terms of differential weathering of plagioclase (in samples with lower CIA than the un-weathered rock, W1-type) and pyroxene (in samples with higher CIA than the un-weathered rock, W2-type) which have varying resistance to weathering. At the hand-specimen scale, the variability in the weathering indices like CIA are controlled by differential weathering of minerals and might not accurately reflect the intensity of weathering. Chondrite-normalized La/Sm and Gd/Lu co-vary with CIA values indicating mobility of the REEs during spheroidal weathering even at the hand-specimen scale. The Eu anomaly also increases with increasing CIA values which is explained by differential weathering of pyroxene and plagioclase. We observe large percentage deviations of the Nb-normalized concentrations of elements from the un-weathered rock in specific samples but no spatial trend is observed. Overall, the variations in element concentrations can be explained by varying fluid mobility of the elements, selective weathering of the minerals in the diabase, and ambient environmental conditions.

Considerable Nd and Sr isotopic variability is observed at the hand-specimen scale and is explained in terms of weathering-related fractionation of parent/daughter ratios. This elemental fractionation must have happened long time ago to allow for radiogenic decay of the long-lived isotopes of ^{87}Rb and ^{147}Sm. The spread (%RSD) in the initial Sr and Nd isotope compositions of the weathered samples reach a minimum value around 1.2–1.3 Ga which we interpret as the timing of the peak weathering event which led to fractionation of the parent/daughter ratios. For Nd isotopes, the average εNd $_{(1.2\ Ga)}$ of the weathered samples coincides with the εNd $_{(1.2\ Ga)}$ of the un-weathered rock. The timing of the weathering event coincides with the timing of the breakup of the Columbia supercontinent and follows wide-spread alkaline volcanism in the Indian subcontinent. This is the first such attempt to determine the timing of a weathering event in rocks using long-lived radioactive isotopes.

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1. Introduction

Silicate weathering is a fundamental process on Earth which consumes atmospheric CO_2 and hence, plays an important role in the regulation of long-term (>1 Ma) climatic conditions (Berner, 1995;

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Berner and Lasaga, 1989, Navarre-Sitchler and Brantley, 2007). During chemical weathering, rock-forming minerals interact with fluids and are converted to secondary minerals leading to loss and/or redistribution of elements. The weathering products of rocks are eventually transported by rivers (as dissolved and suspended loads) and are a major source of cations to the oceans (e.g., Whitfield, 1982). A common type of weathering process in rock outcrops is spheroidal weathering which is used to describe the characteristic formation of concentric layers or shells around a less weathered central core stone; this onion-skin like weathering pattern has been observed on a wide range of rock types like basalt, granite, andesite, sandstone, and schist in diverse modern-day climatic conditions (Fletcher et al., 2006; Jamtveit et al., 2011; Ollier, 1971; Royne et al., 2008). Spheroidal weathering is most commonly seen in rocks which are dominantly composed of plagioclase, olivine, and pyroxene, and is initiated by fluids which percolate through fractures and joints thereby enhancing chemical reactions. Change in chemical compositions, like the hydration of alumina and iron in silicate minerals, cause an increase in volume and expansion of the outer shells, which in turn applies stress causing fractures, and the outer layers to peel off (Buss et al., 2008; Jamtveit et al., 2009; Royne et al., 2008). A coupling between physical and chemical weathering leads to hierarchical fracturing and ultimately, layer-by-layer spalling (Royne et al., 2008). Chemical weathering advance rates vary with equilibrium solubility and pore fluid velocities and are not affected by reaction kinetics in the case of transport-limited weathering (Brantley et al., 2011).

Basalts, which are primarily composed of minerals like plagioclase and pyroxene, readily weather and have consequently been the focus of many studies on element mobility and changes in isotopic composition during chemical weathering at the outcrop scale (e.g., Aiuppa et al., 2000; Hill et al., 2000; Ma et al., 2006; Ma et al., 2007; Ma et al., 2010; Nesbitt and Wilson, 1992; Taylor and Lasaga, 1999; Wimpenny et al., 2007). Most of these studies have focussed on geologically recent weathering profiles that have developed on Phanerozoic-age rocks.

In this study, we investigated the anatomy of a spheroidally weathered diabase of early Proterozoic age at the hand-specimen scale. We performed detailed imaging of the sample to trace the fractures inside the rock, followed by careful micro-sampling and a detailed geochemical and isotopic investigation to evaluate the spatial extent of geochemical and isotopic heterogeneity that may be induced due to spheroidal weathering. We show that elemental concentrations as well as radiogenic Nd, Sr isotopic compositions can vary significantly over small spatial scales of a few centimeters in weathered rocks. Our results provide deeper insight into the process of spheroidal weathering and how it affects the distribution of elements as well as radiogenic isotopic ratios over small spatial scales. Using the Nd, Sr isotopic data we attempt to constrain the timing of the peak weathering event.

2. Sampling

A spheroidally weathered diabase (synonymously used as dolerite or microgabbro) sample, approximately 30 cm in diameter, and part of a dike, was collected from a quarry (12°01.668′N, 77°03.815′E) near the village of Yeragumballi, WSW of Hennur, Karnataka, India. An un-weathered sample of the dike was also collected for geochemical comparison. These dikes are well studied in terms of their mineralogy, petrography, bulk chemistry, and paleo-magnetism and have a U-Pb baddeleyite age of 2367 ± 1 Ma (French and Heaman, 2010; Halls et al., 2007; Kumar et al., 2012). Major element data indicate that these dikes are iron-rich tholeiites, dominantly consisting of clinopyroxene and plagioclase with minor amounts of amphibole, orthopyroxene, biotite and magnetite (Halls et al., 2007). Plagioclase in these rocks shows a brown to black colored clouding which was first reported by Pichamuthu (1959) and is explained by exsolution of magnetite from feldspar due to slow cooling at great crustal depths (Halls et al., 2007; Halls and Zhang, 1995). No intrusion of other rock types is found in this locality and hence, variations in elemental and isotopic

compositions of the diabase are expected to be solely due to spheroidal weathering.

3. Analytical methods

The spheroidally weathered diabase sample was cut to a dimension of 6.3 cm × 6.0 cm × 2.5 cm such that multiple weathering layers could be sampled from the surface (rim) to the interior (core). Micro-computed tomography imaging of a representative portion of this sample was carried out using an X-ray microscope (VersaXRM-510, Xradia, Zeiss, USA). A parallelepiped-shaped sample of dimension ~3.0 cm × ~1.7 cm x ~ 1.4 cm, was scanned with isotropic voxel size of 2.5 μm. A total of 3201 projections with a field of view (FOV) 2532.5 μm × 2532.5 μm were acquired, where the exposure time for each projection was 5 s. The source voltage was 140 kV and power was10 W with transmission and intensity count of 18–27% and 3000–8000, respectively. Reconstruction of collected radiographs was done in XMReconstructor with a Gaussian filter (kernel size 0.7). The reconstructed tomogram was further processed and visualized using Avizo Fire 8.1 (FEI, Bordeaux, France). A non-local-means filter was applied to the raw tomogram, which preferentially removes noise from the image while preserving the edges. The representative 2D images (Fig. 1 d–g), were taken as one voxel thick slices at three orthogonal planes denoted as XY, XZ and YZ.

Powdered samples from 21 layers, from the surface to the interior of the sample were obtained using a hand-held micro-drill with a diamond drill bit (Figs. 1a, b). The samples are numbered based on their average radial distance from a reference point placed towards the core of the sample (Fig. 1c, Supplementary Table 1); sample number 1 is the outermost sample (closest to the rim) and sample number 21 is the innermost (closest to the core) (Fig. 1b, c). Approximately 30–50 mg of sample powder was drilled from each layer. One gram of the un-weathered diabase was crushed using an agate mortar and pestle. For elemental concentration determination, ~25 mg of each sample was dissolved in 15 ml screw-cap Teflon vials from Savillex, USA, using a mixture of 1 ml concentrated HF and 1 ml concentrated HNO_3 acids at 120 °C. After 24 h of reaction, the acid mixture was evaporated and a mixture of 1 ml concentrated HNO_3 and 1 ml concentrated HCl was added to the sample. After another 24 h of reaction at 120 °C, the acids were evaporated and the residue was dissolved in 2 ml of HNO_3 and transferred to 125 ml pre-cleaned HDPE bottles (Tarsons, India). One ml of 1 ppm Be, In, Cs and Bi (internal standards, prepared from 1000 ppm Spec pure ICP solutions, Alfa Aesar) was added to the bottle and the solution was brought up to 100 ml by adding 18.2 MΩ water such that all sample, standard and blank solutions had ~10 ppb internal standards. All sample powders and solutions were weighed such that the dilution factor was ~4000 for all standards and samples. Sample preparation was done in a class 100 laminar flow work area in a class 10,000 clean room at the Center for Earth Sciences (CEaS), Indian Institute of Science (IISc), Bangalore. We used Suprapur grade Hydrofluoric acid from Merck and Emsure brand (ACS, Reag. Ph Eur) nitric and hydrochloric acids, also from Merck. The nitric and hydrochloric acids were further distilled using a Savillex DST-1000 sub-boiling still before use. Our acid blanks are <1 ppt for the REEs, <1 ppb for most other elements and <10 ppb for some major elements like Na. The 18.2 MΩ water was prepared using a Sartorious Stedim - Arium Pro VF filtration unit. The supply-water was filtered using additional coarse filters (5, 3, and 1 μm) prior to introduction into the above unit.

Element concentrations were measured using a quadrupole Inductively Coupled Plasma Mass Spectrometer (ICPMS, Thermo Scientific X-Series II) at CEaS, IISc equipped with Nickel sample and skimmer cones. Samples were introduced using a 100 μm/min PFA nebulizer connected to a peristaltic pump running at 30 rpm into an ESI-PC3 Peltier cooled spray chamber. A CETAC ASX-520 auto-sampler was used. Uptake time for samples and standards was 60 s while the rinse time (in 2% HNO_3) was 90 s. A 10 ppb internal standard with Be, Cs,