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Dating of chemical weathering processes by *in situ* measurement of U-series disequilibria in supergene Fe-oxy/hydroxides using LA-MC-ICPMS

J.P. Bernal [a,b,*], S.M. Eggins [a], M.T. McCulloch [a], R. Grün [a], R.A. Eggleton [b]

[a] *Research School of Earth Sciences, The Australian National University, Canberra, ACT 0200, Australia*
[b] *CRC-LEME. Department of Earth and Marine Sciences, The Australian National University, Canberra, ACT 0200, Australia*

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Abstract

Constraints on the timing of weathering processes in the northern Australian regolith have been obtained by *in situ* measurement of U-series disequilibria in U-rich supergene Fe-oxy/hydroxides using a laser ablation-MC-ICPMS technique. This approach has permitted the measurement of $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ activity ratios in finely crystalline Fe-oxy/hydroxides from the Ranger uranium deposit with sufficient precision and spatial resolution to constrain the age of formation of these phases and to develop a geochronological framework for weathering processes.

$^{230}Th/^{238}U$ systematics in the finely crystalline Fe-oxy/hydroxides yield ^{230}Th-ages ranging from 60 to 350 ka. The most reliable ^{230}Th-ages cluster between 122 and 216 ka, suggesting Fe-oxy/hydroxides formation and associated weathering, peaked during the previous 2 interglacial periods. This is supported by the ^{230}Th-ages and isotope composition of pisolith (Fe-oxy/hydroxide pedogenic nodules) cores which are demonstrated to behave as closed systems. The U isotopic composition of the Fe-oxy/hydroxides is consistent with an origin from groundwater in equilibrium with dissolved uraninite. Secondary overprinting is evident in some samples as a large range in $^{234}U/^{238}U$. Our results suggest that weathering intensity varies with global climate cycles and that, together with weathering events dated by $^{40}Ar/^{39}Ar$ of Mn-oxides elsewhere in northern Australia ([Feng, Y.X. and Vasconcelos, P., 2001. Quaternary continental weathering qeochronology by laser-heating $^{40}Ar/^{39}Ar$ analysis of supergene cryptomelane. Geology, 29(7): 635–638.]), weathering rates in this region are orbitally forced.

Keywords: Weathering; Fe-oxy/hydroxides; LA-MC-ICPMS; U-decay series; Northern Australia; Orbital forcing

1. Introduction

Chemical weathering and magmatism are the two principle processes responsible for elemental differentiation in the Earth's crust (Berner, 1985). However, unlike magmatic differentiation, comparatively little is known about the rates and timing of weathering, its dynamics, or the effects of varying climatic and geochemical conditions that might sustain, enhance or even interrupt weathering processes. This is particularly relevant in the context of the Australian continent, since the vast majority of its surface is covered by one or more forms of regolith, such as saprolite, duricrust and/or aeolian deposits.

* Corresponding author. Present address: Departamento de Geoquímica, Instituto de Geología, Universidad Nacional Autónoma de México, Ciudad Universitaria, Mexico City, 04510 Mexico. Tel.: +52 55 56224285; fax: +52 55 56224317.
E-mail address: jpbernal@geologia.unam.mx (J.P. Bernal).

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Weathering minerals are chemically complex. They are usually poorly crystalline, embedded within complex mineral textures, and difficult to separate by physical means; consequently isotope analysis of weathering minerals is difficult. Analysis of bulk-weathered-rocks yields isotopic signatures that can be difficult to interpret and, in some cases, can provide information regarding radionuclide mobilization events but not their exact timing (e.g. Mathieu et al., 1995; Dequincey et al., 2002; Chabaux et al., 2003). Moreover, the use of chemical pre-treatments or selective extractions usually cause elemental and isotopic fractionation (Shulmeinster et al., 1993). Such limitations can be addressed, however, by using microsampling techniques, such as laser-ablation (LA) or microdrilling. These techniques can provide texturally controlled results for discrete mineral phases and, consequently, a basis for understanding the micro-scale geochemical environment affecting them. Microsampling is notable for having facilitated the dating of supergene Mn-oxides using K–Ar and ^{40}Ar–^{39}Ar systematics (e.g. Vasconcelos, 1999; Vasconcelos and Conroy, 2003; Colin et al., 2005), and the establishment of a geochronological framework for associated weathering processes.

Despite recent advances in weathering geochronology using radiogenic isotopic systems (such as K–Ar, ^{40}Ar/^{39}Ar, U–Th/He) coupled with microsampling methodologies, few results have constrained weathering processes during the Late Quaternary (<500 ka) in Australia (Dammer et al., 1999; Feng and Vasconcelos, 2001). This represents a significant gap in our understanding of weathering processes, particularly during the Quaternary, where the record of climatic variation is more extensive and better preserved than other periods, and for which the greatest potential exists for assessing the role of global climate change on weathering processes.

In this study ^{238}U-series disequilibria in authigenic Fe-oxy/hydroxides (goethite—α-FeOOH and hematite—α-Fe_2O_3) is assessed as a geochronological recorder of weathering processes. Authigenic Fe-oxy/hydroxides commonly occur as weathering products of ferrous minerals, and have high affinities for dissolved uranyl complexes (Ames et al., 1983; Hsi and Langmuir, 1985; Sato et al., 1997; Bargar et al., 2000; Duff et al., 2002). Furthermore, ^{230}Th is generally fractionated from its parent ^{234}U during weathering, effectively "resetting" the ^{230}Th/U geochronometer (Osmond and Ivanovich, 1992).

U-series isotopes have been previously measured in Fe-oxy/hydroxides facies using bulk-rock α-spectrometry combined with selective dissolution methods to constrain radionuclide mobility (Lowson et al., 1986; Short et al., 1988; von Gunten et al., 1999) and to date the precipitation of Fe-oxy/hydroxide concretions (Short et al., 1989; Shulmeinster et al., 1993; Augustinus et al., 1997). However, besides the sample-size limitations of α-spectrometry, selective dissolution methods often do not produce reliable ^{230}Th-ages due to elemental fractionations induced by partial dissolution of mineral phases not intended to be attacked by the leaching agent (Shulmeinster et al., 1993), and the formation of mixing arrays which have no age significance. In this paper, we present U-series disequilibria data for Fe-oxy/hydroxides measured by laser-ablation MC-ICPMS, which suggest these finely crystalline supergene Fe-oxy/hydroxides often display closed system behaviour for U and Th and, thus, can provide information on the timing of weathering processes as well as insights into processes controlling weathering rates.

2. Experimental

2.1. Samples

Samples analysed in this work are Fe-oxy/hydroxides formed by the weathering of a chlorite–muscovite schist. These were collected from the Ranger Uranium Mine orebody # 3, Jabiru, NT, Australia (Fig. 1), where weathering profiles have been developed in a U-rich protolith and recently exposed by mining activities. The Ranger orebodies occur along with the Koongarra, Nabarlek, and Jabiluka U-deposits, and numerous other radiometric anomalies, within the Pine Creek Geosyncline (Ewers and Ferguson, 1980). The bedrock (chlorite–muscovite schist) has undergone extensive weathering, and most Fe-oxy/hydroxides along with kaolinite, vermiculite and smectite present in the regolith have been formed by *in situ* alteration of chlorite (Bernal, 2003). Weathering appears to have proceeded broadly in a downward direction since a more advanced state of alteration is observed at the top. However, the weathering front and groundwater flow is clearly influenced by the rock schistosity. The saprolite is covered by a ferruginous duricrust (ferricrete) 1–3 m thick, which shows no fabric or textural continuity with the weathered schist underneath. Pisoliths are ubiquitous on the duricrust's upper surface.

Approximately 1–2 kg of saprock and saprolite samples were collected at different heights from 3 different weathering profiles, and taken from depths into the wall of approximately 20–30 cm in order to minimise any recent alteration of the samples following exposure by mining. Fifty ferruginous pisoliths and nodules were hand-picked from the ferricrete layer at the surface of the