Weathering geochronology by (U-Th)/He dating of goethite

DAVID L. SHUSTER,1,* PAULO M. VASCONCELOS,2 JONATHAN A. HEIM2 and KENNETH A. FARLEY1
1Division of Geological and Planetary Sciences, MC 100-23, California Institute of Technology, Pasadena, CA 91125, USA
2Department of Earth Sciences, University of Queensland, Brisbane, Queensland 4072, Australia

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Abstract—Nine samples of supergene goethite (FeOOH) from Brazil and Australia were selected to test the suitability of this mineral for (U-Th)/He dating. Measured He ages ranged from 61 to 8 Ma and were reproducible to better than a few percent despite very large variations in [U] and [Th]. In all samples with internal stratigraphy or independent age constraints, the He ages corroborated the expected relationships. These data demonstrate that internally consistent He ages can be obtained on goethite, but do not prove quantitative He retention. To assess possible diffusive He loss, stepped-heating experiments were performed on two goethite samples that were subjected to proton irradiation to produce a homogeneous distribution of spallogenic 3He. The 3He release pattern indicates the presence of at least two diffusion domains, one with high helium retentivity and the other with very low retentivity at Earth surface conditions. The low retentivity domain, which accounts for ~ 5% of 3He, contains no natural 4He and may represent poorly crystalline or intergranular material which has lost all radiogenic 4He by diffusion in nature. Diffusive loss of 3He from the high retentivity domain is independent of the macroscopic dimensions of the analyzed polycrystalline aggregate, so probably represents diffusion from individual micrometer-size goethite crystals. The 3He/4He evolution during the incremental heating experiments shows that the high retentivity domain has retained 90%–95% of its radiogenic helium. This degree of retentivity is in excellent agreement with that independently predicted from the helium diffusion coefficients extrapolated to Earth surface temperature and held for the appropriate duration. Considering both the high and low retentivity domains, these data indicate that one of the samples retained 90% of its radiogenic 4He over 47.5 Ma and the other retained 86% over 12.3 Ma. Thus while diffusive-loss corrections to supergene goethite He ages are required, these initial results indicate that the corrections are not extremely large and can be rigorously quantified using the proton-irradiation 3He/4He method. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

Weathering profiles provide a record of chemical and physical processes occurring at the surface of terrestrial planets. Their mineralogical and geochemical compositions record information on the composition and abundance of weathering solutions, and their depth and complexity provide insight to the longevity of their development and the role that climate and biologic processes have in enhancing weathering processes. The global distribution of weathering profiles reflects rainfall and temperature gradients across the planet. The profiles also reflect the balance between chemical-physical weathering and chemical-physical erosion, providing insight into landscape evolution and global geochemical cycles.

The thermodynamic stability and slow dissolution kinetics of many supergene minerals found in weathering profiles favors their preservation under earth surface conditions, making them useful recorders of paleoenvironmental conditions. Because deeply weathered profiles occur on most continents and appear to have formed over a wide range of geologic times, they potentially represent a powerful record of continental paleoenvironments. Savin and Epstein (1970) first proposed the combined use of O and H isotope systematics in weathering minerals to reconstruct continental paleoclimates. Experimentally determined O and H isotopic fractionation factors have been widely applied to quantify paleotemperatures during goethite and kaolinite precipitation (Yapp, 1987; Yapp, 1990; Bird and Chivas, 1993; Lawrence and Meaux, 1993; Girard et al., 1997; Giral-Kacmarcik et al., 1998; Girard et al., 2000; Yapp, 2000). Yapp (2000) demonstrated that supergene goethite (FeOOH) can behave as a closed system with respect to O and H exchange for at least ~50 Myr. Despite the wealth of information recorded in weathering profiles, their usefulness as paleoclimatic and paleoenvironmental indicators is limited by the paucity of information on their timing and rate of formation.

An understanding of weathering profile evolution and derivation of paleoclimatic information from these potential archives requires quantitative knowledge of the timing of specific weathering reactions and measurements of the rate of propagation of weathering fronts. Advances have recently been made in these areas (Vasconcelos et al., 1992; Brown et al., 1994; Vasconcelos et al., 1994b; Dequincey et al., 1999). In young weathering profiles (<1 Ma), weathering geochronology by U-Th decay series dating of pedogenic carbonate and silica minerals provides reliable information on timing of mineral precipitation (Sharp et al., 2003). In older weathering profiles hosting supergene K-bearing minerals, weathering geochronology by the K-Ar and 40Ar/39Ar methods are useful. Vasconcelos et al. (1994a, 1994b); Dammer et al. (1996, 1999); Ruffet et al. (1996); Hénocque et al. (1998); Hautmann and Lippolt (2000) applied 40Ar/39Ar dating to K bearing Mn-oxides (cryptomelane) and sulphates (alunite-jarosite) from profiles in South America, Africa, Australia, and Europe. Precipitation ages ranging from ~70 Ma to modern suggest that some continental weathering profiles have been continuously ex-

* Author to whom correspondence should be addressed (dshuster @caltech.edu).
posed at least since the Cretaceous. Dequincey et al. (2002) measured major and trace element abundances and $^{238}$U-$^{234}$U-$^{230}$Th activity ratios in bulk rock samples from a 15-m-thick African lateritic profile. They found evidence of recent U mobility throughout the laterite, possibly initiated by a late Pleistocene climatic shift, and suggested two episodes of laterite formation. In situ produced cosmogenic nuclides have also been used to constrain the mechanisms of weathering profile development (Brown et al., 1994; Braucher et al., 1998; Braucher et al., 2000). Braucher et al. (2000) interpreted homogeneous $^{10}$Be and $^{26}$Al concentrations in quartz in the uppermost $\sim$2 m and an exponential decrease in the lower $\sim$8 m of a 10 m lateritic soil profile to indicate bioturbation of the surface layer. Small et al. (1999) and Riebe et al. (2003) used the accumulation of $^{10}$Be and $^{26}$Al, combined with mass balance calculations, to infer rates of regolith production.

Lateritic weathering profiles, often more than 400 m thick, host a plethora of supergene iron minerals distributed from the surface (in loose pisoliths and ferruginous durricrusts), through the mottled zone, and down into the saprolite and the weathering-bedrock interface. These lateritic profiles are texturally and geochemically complex and it is difficult to distinguish between relict features and those resulting from ongoing processes. A variety of geochemical and petrological tools have been employed to characterize the superimposed horizons (ferricrete, mottled zone, saprolite, etc.) common to complete lateritic weathering profiles (e.g., Anand and Paine, 2002). In detail, these studies reveal that lateritic profiles represent the result of successive and ongoing geochemical, geomorphological and biologic processes. The great depth and complexity of lateritic weathering profiles, combined with the abundance of supergene iron minerals throughout the profile, suggest that the development of a methodology suitable for dating supergene iron oxides and hydroxides may significantly improve our understanding of the paleoclimatic and environmental conditions controlling continental weathering.

Because weathering products usually precipitate and reside at near surface temperatures, and because such conditions are favorable for slow helium diffusion, we have investigated whether radiogenic helium is quantitatively retained in supergene goethite. If $^4$He, U and Th are immobile in a mineral produced via weathering, the (U-Th)/He age represents the time since its precipitation. Due to its rapid radiogenic evolution, the (U-Th)/He system offers potential to date, to high resolution, a variety of supergene minerals that contain even trace amounts of U and/or Th over a range of timescales ($\sim$0.5 Ma to $\sim$100s Ma).

The application of (U-Th)/He dating to Fe-oxides is not a new idea, but has recently come under renewed study. Strutt (1910) reported the first He age measured on a limonite ($\sim$2Fe$_2$O$_3$ $\cdot$ 3H$_2$O; $\sim$140 Ma). More recently, Lippolt and others reported a dozen He ages on hydrothermal and supergene goethites (FeOOH), limonites (Lippolt et al., 1998) and hydrothermal hematites (Fe$_2$O$_3$) (Wernicke and Lippolt, 1993; Baehr et al., 1994; Wernicke and Lippolt, 1994a; Wernicke and Lippolt, 1994b; Lippolt et al., 1995) from central Europe. The reported hematite He ages are as young as $\sim$5 Ma and as old as $\sim$180 Ma. Helium-4 diffusion experiments (Baehr et al., 1994; Wernicke and Lippolt, 1994a), comparisons with coexisting adularia and biotite K/Ar ages and tests for internal consistency (Lippolt et al., 1995) all indicate that geologically significant He ages can be determined on certain samples of hydrothermal hematite. The goethite He ages determined by Lippolt et al. (1998) span from $\sim$0.8 Ma to $\sim$130 Ma, qualitatively indicating helium retention over geologic timescales. They concluded that (U-Th)/He dating of goethite is potentially useful for dating very young crustal movements. However, a quantitative description of helium diffusivity in these materials at Earth surface conditions is required to establish the significance of these ages.

In this work, we evaluated the helium retentivity of polycrystalline aggregates of supergene goethite (FeOOH). We chose goethite due to its ubiquity, because it often contains high uranium concentrations in the weathering environment (Giammer, 2001), and because U in goethite may occupy well defined crystallographic sites (Duff et al., 2002). Our approach was both empiric and experimental. The empiric approach tested He age reproducibility and U and Th concentration homogeneity on multiple aliquots of individual samples. We also compared Fe-oxide He ages with cryptomelane 40Ar/39Ar ages from the same weathering profiles, one directly associated goethite/cryptomelane pair, and of regionally associated samples. The experimental approach involved vacuum diffusion experiments on proton-irradiated polycrystalline goethite to determine the temperature dependence of helium diffusivity, from which we were able to characterize $^4$He retentivity at Earth surface temperatures. We conducted stepwise degassing experiments in which we measured both the natural radiogenic $^4$He and the spallogenic $^3$He induced by proton bombardment (Shuster and Farley, 2004; Shuster et al., 2004).

2. SAMPLES

For this study, we selected goethite based on several criteria: (1) in most cases, they were precipitated directly from weathering solutions into cavities created by the dissolution of primary sulfides or carbonates; (2) they exhibited botryoidal growth habits recording relative timing of mineral precipitation; (3) they were pure and devoid of primary contaminants; (4) they were composed of aggregated goethite crystallites ($<1 \text{ \mu m}$); (5) they were associated with other datable supergene phases (i.e., cryptomelane), and their relative timing of precipitation could be determined based on textural relationships. Efforts were taken to ensure that aliquots of each sample were from a single generation of goethite. Two samples were then selected for detailed stepwise degassing diffusion experiments. We briefly describe the nine goethite samples below.

The four Bahia goethites (BAH-F124-111.2, 114, 118, and 123) are vitreous, botryoidal, of high purity, and precipitated from solution into empty cavities, which based on their morphology are known to have created during the dissolution of primary pyrite, chalcopyrite, and calcite (Fig. 1). Because these samples precipitated from solution, they are unlikely to have contained detrital grains of un-weathered $^4$He bearing phases. The four samples were collected from a drill core from the weathering profile associated with the Igarapé Bahia Cu-Au deposit, Carajás, Brazil, from a drill-hole depth of $\sim$110–120 m, equivalent to a vertical depth of ca. 80 m below the present surface; they precipitated and subsequently resided at depth throughout their existence. Multiple aliquots of samples 111.2...
and 114 were prepared for He age reproducibility tests. Small pieces of the goethite bands were broken off, and then further divided into aliquots for multiple analyses. For instance BAH-F124-114-(a) is a ~10 mg piece of the BAH-F124-114 goethite growth band and BAH-F124-114-(a)-1 is one of the 9 subaliquots prepared for analysis from that piece. Likewise BAH-F124-114-(b) is another piece sampled from the same growth band. We expect that each aliquot has approximately the same precipitation age. Figure 1b shows that the crystallites are ~0.5 μm in their minimum dimension.

The MI-2000-09 sample comes from a gossan at the Lake Moondarra Cu-prospect in the Mount Isa region, NE Australia. The sample is also associated with cavities formed in a quartz veins by the dissolution of primary sulfides and carbonates during weathering reactions. These cavities often contain iron and manganese oxides and hydroxides. Several cryptomelane samples from a nearby outcrop and another outcrop in the same area, have been previously dated by the 40Ar/39Ar method (Vasconcelos, 1998).

Sample B01-009 is a 15 cm hand specimen from the N4E iron mine in Carajás, Brazil. The sample is from the surface “canga,” or lateritic iron ore associated with weathering of the Carajás banded iron formation. We analyzed four subsamples of B01-009 (labeled a,c,e,g) that were texturally identified as four distinct generations of goethite present in the sample. Paragenetic relationships expressed in the hand sample suggest precipitation ages decrease in the order a,c,e,g.

3. METHODS

3.1. He Dating

Using isotope-dilution mass spectrometry, we measured both [3He] (quadrupole), and [230Th] and [232Th] (double-focusing ICP-MS) of individual sample aliquots. We extracted He from relatively larger aliquots (~200 μg) using a resistance furnace, and from smaller aliquots (~5 μg) using laser extraction. Details of the analytical techniques used for this study are described in Farley (2002) but modified as follows.

Because the individual goethite crystals are extremely small (~1 μm), the analyzed chips represent aggregates of ~10^3 individual crystals. To eliminate the effects of a ejection (Farley et al., 1996), we selected interior aliquots from mm-size botryoidal clusters. We verified mineral identification and ensured sample purity using Raman spectroscopy and powder X-ray diffractometry (XRD). The analyzed samples were greater than 99% FeOOH. Before analysis, we rinsed the aliquots in alcohol using sonication to remove small particulates adhered to the sample surfaces. To ensure quantitative transfer for U and Th analysis, we encapsulated the aliquots in Pt foil packets and used furnace and laser extraction temperatures of ~1150°C. Following He extraction, we dissolved the Fe oxides in 200 μL of concentrated HCl and heated for 12 hours to 90°C. 230Th and 235U spikes were added during dissolution.

For the He age calculations, we assumed (1) secular equilibrium among daughter nuclides in the 238U series; (2) a closed system for parents and daughters; and (3) zero initial He at the time of precipitation; these assumptions will be discussed below. Aliquots for furnace extraction were weighed before analysis to permit calculation of parent and daughter concentrations. For laser extraction, the masses of the Fe oxides were estimated by measuring the Fe concentration in solution. Because these masses are fairly uncertain, the concentrations are only approximate; however note that calculated He ages are independent of mass.

3.2. Step-Heating Diffusion Experiments

Details of the stepwise degassing method used in this study were described by Shuster et al. (2004). The samples were held at a known temperature (T) for a known amount of time (τ) in a volume of ~300 cm³ under static vacuum. Following a heating step, the accumulated He and 4He were measured by sector field mass spectrometry using external standard calibration.

We converted measured helium release-fractions to diffusion coefficients (D/dt where a is the diffusion domain radius) for each temperature step assuming spherical geometry (Fechtig and Kalbitzer, 1966). The calculation assumes an initially uniform spacial distribution of the diffusant. This assumption may not be valid if diffusion has affected the radiogenic 4He distribution; a diffusively modified 4He distribution will yield underestimates of D/dt by this method.

To test for potential 4He losses, we bombarded our samples with ~10^14 protons/cm² using a ~150 MeV proton beam at the Harvard Cyclotron Laboratory to generate a uniform distribution of spallogenic 4He. Shuster et al. (2004) showed that proton bombardment yields a spatially uniform 4He distribution across individual crystals as large as ~180 μm, and that, at least for apatite and titanite, the irradiation itself...
The listed He age uncertainties are 1σ propagated from U, Th and 4He analytical uncertainties and underestimate true He age uncertainties. The U, Th and 4He concentrations are approximations; calculated He ages are independent of mass. nmol is $10^{-9}$ moles, “n.d.” denotes not determined.

4. HELIUM DATING—RESULTS

The measured [4He], [U], and [Th] and resulting goethite He ages are listed in Tables 1 and 2. Table 1 shows replicated analyses of samples 111.2 and 114, and Table 2 summarizes all of the goethite He ages and their comparator Ar ages. We measured 3He/4He ratios on non-irradiated aliquots of these samples to be effectively zero ($<2 \times 10^{-8}$), indicating only radiogenic helium.

We observed a wide range in concentrations of [4He], [U], and [Th]; from $~0.04$ to 23 nmol/g, 0.3 to 370 ppm, and $<0.01$ to 3.4 ppm, respectively. He ages range from $~61$ to $~8$ Ma. Th/U ratios are low ($<0.1$) for all goethite samples except those collected from the uppermost few meters of ferricrete from the N4E iron mine, Carajás, Brazil (B01-009 series), that have Th/U ranging from 2 to 10. The ranges in [U] and [Th] of eleven aliquots of sample 111.2 span factors of 4 and 44, respectively. We measured [4He] on six of these aliquots; the He ages differ by $~1.3\%$ (42.6 ± 0.5 Ma; n = 6). The [4He] and [U] of sample 114 span factors of 23 but the He ages vary by only 2% (10.7 ± 0.2 Ma; n = 23). The He ages of the four B01-009 aliquots (a,c,e,g) also corroborate their paragenetic relations. As expected, the aliquot identified to be the youngest gave the youngest He age (8.3 Ma) and the oldest gave the oldest He age (61 Ma).

4.1. Comparing He Ages with Ar Ages

The best way to test the accuracy of an absolute geochronometer is to compare it against an independently known mineral precipitation age. However, there are no other tech-
Weathering geochronology by (U-Th)/He dating of goethite

Table 2. Comparison between He and Ar ages, stratigraphic relationships.

<table>
<thead>
<tr>
<th>Region:</th>
<th>phase</th>
<th>Sample</th>
<th>Radiometric age (Ma)</th>
<th>[U] (ppm)</th>
<th>[Th] (ppm)</th>
<th>[³²He] (nmol/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bahia:</td>
<td>goethites</td>
<td>BAH-F124-111.2*</td>
<td>(U-Th)/He</td>
<td>42.62</td>
<td>0.53</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>goethites</td>
<td>BAH-F124-118</td>
<td>30.38</td>
<td>0.34</td>
<td>29.39</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>goethites</td>
<td>BAH-F124-123</td>
<td>15.80</td>
<td>0.18</td>
<td>29.00</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>goethites</td>
<td>BAH-F124-114*</td>
<td>10.67</td>
<td>0.21</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>goethites</td>
<td>B01-009-(a)</td>
<td>61.02</td>
<td>0.61</td>
<td>0.76</td>
<td>3.43</td>
</tr>
<tr>
<td></td>
<td>goethites</td>
<td>B01-009-(c)</td>
<td>36.87</td>
<td>0.37</td>
<td>0.26</td>
<td>2.52</td>
</tr>
<tr>
<td></td>
<td>goethites</td>
<td>B01-009-(e)</td>
<td>26.70</td>
<td>0.27</td>
<td>0.65</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>goethites</td>
<td>B01-009-(g)</td>
<td>8.33</td>
<td>0.08</td>
<td>0.36</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>cryptomelanes</td>
<td>B01-009-(a)</td>
<td>10.67</td>
<td>0.21</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>cryptomelanes</td>
<td>B01-009-(c)</td>
<td>61.02</td>
<td>0.61</td>
<td>0.76</td>
<td>3.43</td>
</tr>
<tr>
<td></td>
<td>cryptomelanes</td>
<td>B01-009-(e)</td>
<td>36.87</td>
<td>0.37</td>
<td>0.26</td>
<td>2.52</td>
</tr>
<tr>
<td></td>
<td>cryptomelanes</td>
<td>B01-009-(g)</td>
<td>26.70</td>
<td>0.27</td>
<td>0.65</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>cryptomelanes</td>
<td>B01-009-(g)</td>
<td>8.33</td>
<td>0.08</td>
<td>0.36</td>
<td>2.00</td>
</tr>
<tr>
<td>Mount Isa:</td>
<td>goethite</td>
<td>MI-2000-09</td>
<td>(U-Th)/He</td>
<td>15.61</td>
<td>0.18</td>
<td>4.27</td>
</tr>
<tr>
<td></td>
<td>goethite</td>
<td>BAH-F124-111.2</td>
<td>0.56</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>cryptomelanes</td>
<td>Regional range</td>
<td>40 to 0</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Notes: The He age uncertainties are 1σ propagated from U, Th and ⁴He analytical uncertainties and underestimate true He age uncertainties. The U, Th and ⁴He concentrations are approximations. Also reported are ⁴⁰Ar/³⁹Ar ages determined on associated cryptomelane, where applicable. nmol is 10⁻⁹ moles.

* Average of replicate analyses (see Table 1).
** Vasconcelos et al., 1994, “-“ not applicable.

Tectonics by which to directly date these minerals. An indirect comparison between different weathering phases is currently the only way to test the accuracy of the goethite (U-Th)/He ages.

The Bahia goethite He ages generally agree with cryptomelane ⁴⁰Ar/³⁹Ar ages from the same profile, which range from ~40 to 0 Ma (Vasconcelos et al., 1994b). The eight goethite He ages in Table 2 fall in approximately this same range (~61 to 8 Ma). In the case of Bahia goethite sample 111.2 (He age ~43 Ma), two nearby samples (111.8 and 112.1) containing cryptomelane overgrowth on botryoidal goethite yield ⁴⁰Ar/³⁹Ar ages of 13.7 ± 0.6 and 13.8 ± 0.3 Ma, consistent with the observed paragenetic relationship. Sample 111.2 contains a generation of cryptomelane that is directly precipitated over the goethite (Fig. 1). We do not necessarily expect that these two phases share a common precipitation age; however the cryptomelane age must be younger than the age of the goethite. The radiometric ages of the cryptomelane/goethite pair are consistent with their paragenetic relationship; the goethite He age is ~43 Ma whereas the three grains of cryptomelane from that sample yield ⁴⁰Ar/³⁹Ar plateau ages of 19.4 ± 0.2 Ma, 20.6 ± 0.2, 19.2 ± 0.3 and 21.6 ± 0.6 Ma.

The He age for the Lake Moondarra sample MI-2000-09 (Table 2; 15.61 ± 0.18 Ma) also agrees well with ⁴⁰Ar/³⁹Ar ages from nearby samples (plateau ages of 20.7 ± 0.3, 19.7 ± 0.1, 19.0 ± 0.4, 16.0 ± 1.7, and 15.2 ± 1.2 Ma). The goethite and cryptomelane samples from the Lake Moondarra locality occur on a regionally recognized ca. 300 m-elevation weathering surface (Vasconcelos, 1998). The age of supergene minerals in some of these surfaces has been locally and regionally correlated (Vasconcelos and Conroy, 2003). Several other samples dated for the same surface in the Mt Isa Mines gossan, ~20 km away from the Lake Moondarra locality, yield cryptomelane ⁴⁰Ar/³⁹Ar plateau ages of 21.5 ± 0.3, 21.2 ± 0.5, 20.9 ± 0.2, 20.7 ± 0.2, 20.02 ± 0.19, 18.0 ± 0.3, 17.7 ± 0.5, 16.7 ± 0.2, and 14.57 ± 0.12 Ma. The (U-Th)/He results obtained for the goethite sample is entirely consistent with the ⁴⁰Ar/³⁹Ar plateau ages of cryptomelane ages from the same weathering profile. Goethite and Mn-oxides in the lake Moondarra site both reflect water-rock interaction during weathering of sulfide-carbonate hydrothermal assemblages. Once goethite and Mn-oxides precipitate, they will remain metastably preserved, particularly if after mineral precipitation the groundwater levels drop, leaving these minerals stranded in the unsaturated zone. A progressive drop of the water table is a predictable consequence of the known aridification of Australia since the Miocene.

5. HELIUM DATING—DISCUSSION

Three important results of the He dating study are that polycrystalline goethite contains (1) variable but generally ppm level concentrations of U and Th; (2) relatively high ³²He; and (3) He ages that are reproducible despite significant inter aliquot variability in [U] and [Th]. The He age reproducibility, particularly despite strong [U] and [Th] variability, indicates systematic behavior in the polycrystalline goethite which precludes significant U and Th mobility (Farley et al., 2002). For example, uniform addition or removal of U from the goethite at some time following precipitation would not yield isochronous He ages in aliquots with variable U concentrations.

Each of the aliquots was originally located ~250 μm from the next nearest aliquot and sampled from single massive generations of goethite. Since some samples have strongly heterogeneous U and Th concentrations between aliquots, commonality in their He ages requires that radiogenic ³²He atoms have not migrated between the aliquots (~125 μm distance) since formation. Radiogenic helium was either quantitatively
Corroboration of the paragenetic age relationship between the cryptomelane (younger) and goethite (older) by the He ages for sample 111.2 is also significant. Because diffusive helium loss and late stage U adsorption are processes likely to disrupt a goethite He age, and because both processes would result in an artificially young age, it is easier to reconcile systematically young He ages than old. Although the apparent ∼20 Myr hiatus between Fe-oxide and Mn-oxide precipitation is initially surprising, the precipitation timescales of coexisting phases are difficult to know a priori, particularly in the complicated processes of chemical weathering. The apparent ∼20 Myr hiatus between Fe-oxide and Mn-oxide precipitation is permissible, and may represent distinct weathering events in that region.

Once incorporated into goethite, the apparent immobility of U and Th implies that the goethite aggregates are resistant to post precipitation changes in groundwater chemistry. De-quincey et al. (2002) found evidence of recent U mobility throughout a lateritic profile in Africa by measuring U series activity ratios of homogenized whole rock samples. Their findings indicated that a recent (0.3 Ma) chemical remobilization had occurred throughout that system. They proposed that 234U could have been removed from the uppermost ferruginous unit (composed primarily of hematite and goethite) and redistributed throughout the lower units of the profile. However, they also proposed that the high apparent 234U/238U fractionations indicated that U was not easily removed from the ferruginous unit and that U would have been mostly retained by Fe oxy-hydroxides. Because our measurements were made on isolated goethite of high purity, it is difficult to compare the results with those of a whole rock analysis. However, if U and Th were at any point mobilized throughout the Bahia profile, then the isochronous goethite He ages require that goethite aggregates acted as a robust closed system with respect to U and Th.

Several important questions arise regarding U and Th spatial variability within the goethite aggregates. U and Th are clearly not homogeneously distributed throughout the samples, although we do not well understand where or how U and Th are incorporated into the goethite aggregates. These parent elements are either incorporated into the goethite structure itself or adsorb onto mineral surfaces and are subsequently trapped into the crystal aggregate by overgrowth. Uranium adsorption onto goethite is an efficient process in groundwater systems (Andersson et al., 1998; Tricca et al., 2000; Giammer, 2001; Tricca et al., 2001), and it is possible that UO2+ adsorbs on goethite through inner-sphere surface complexes (Gabriel et al., 1998; Bargar et al., 1999; Giammer, 2001) or precipitates as minor amounts of U-phosphate, U-vanadate, or in another U-bearing supergene phase. Recent experimental investigation on uranium co-precipitation with synthetic iron oxides provides compelling evidence that U is incorporated into goethite structures and is not simply adsorbed onto mineral surfaces (Duff et al., 2002). The more limited aqueous mobility of Th in low-temperature groundwater suggests that any significant Th concentration may reflect inheritance of Th from primary minerals.
Table 3. Stepwise degassing results.

<table>
<thead>
<tr>
<th>Step</th>
<th>T (°C)</th>
<th>t (hr)</th>
<th>(^3)He (× 10^6 atoms) (+/−)</th>
<th>(^4)He (× 10^9 atoms) (+/−)</th>
<th>Step</th>
<th>T (°C)</th>
<th>t (hr)</th>
<th>(^3)He (× 10^6 atoms) (+/−)</th>
<th>(^4)He (× 10^9 atoms) (+/−)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>5</td>
<td>0.29 0.02</td>
<td>BDL BDL</td>
<td>1</td>
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LS = last step, BDL = below detection limit.

The stepwise \(^3\)He and \(^4\)He degassing results used to calculate diffusion coefficients shown in Fig. 2 for Bahia goethite samples 114 and 111.2. Uncertainties in atomic abundance are reported at the 95% confidence level. All temperatures were controlled to better than 1 °C. LS = last step, BDL = below detection limit.
low $^3$He/$^4$He ratios of these samples, the proton irradiation effectively generated a purely synthetic distribution of $^3$He in samples containing a natural distribution of only $^4$He. Spallogenic helium produced via proton bombardment has a $^4$He/$^3$He ratio of $\sim 10$, contributing a negligible component to the $^4$He budget of each sample. For this reason, we can consider the experimental results of each isotope separately, as each should provide distinct information about the sample (Shuster and Farley, 2004; Shuster et al., 2004). We present diffusion coefficients calculated from the measured release fractions of proton-induced $^3$He in Figure 2 and radiogenic $^4$He in Figure 3. Due to the possibility of diffusive rounding, values of $\ln(D/a^2)$ calculated from $^4$He release fractions may not accurately...
reflect diffusivity. We therefore concentrated on $^{3}$He to quantify helium diffusion coefficients and $^{4}$He to determine the degree of partial $^{4}$He retention. Note that the heating schedules of these experiments included both prograde (sequentially increasing) and retrograde (decreasing) steps.

6.1. Proton-Induced $^{3}$He Diffusion Parameters

The most apparent feature of the $^{3}$He results is a break in slope occurring at $\sim$180°C that separates two distinct arrays (Fig. 2). The array of higher diffusivity was obtained from the initially derived gas, and amounts to 4 and 8% of the total $^{3}$He budgets of samples 114 and 111.2, respectively. Note that points on an Arrhenius plot are not weighted according to the amount of extracted gas. For example, although the higher diffusivity arrays have strong graphical representation, the steps cumulatively represent small proportions of the total $^{3}$He budgets.

This type of feature has been observed in other phases using both proton-induced $^{3}$He and radiogenic $^{4}$He, and suggests that multiple diffusion domains are present in the samples (Reiners and Farley, 1999; Reiners et al., 2004; Shuster et al., 2004). Although these data have important implications discussed further below, the arrays of lower diffusivity, representing the majority (>90%) of the extracted $^{3}$He, better characterize helium diffusivity in the bulk of the polycrystalline samples. These arrays have strong linear correlations between $\ln(D/a^2)$ and $1/T$ between 145°C and 225°C with correlation coefficients ($R^2$) higher than 0.996 for each experiment. The correlations persist throughout retrograde temperature cycles indicating that (1) during those steps $^{3}$He is derived primarily from a single characteristic domain size, and (2) the assumed initial uniform $^{3}$He distribution is valid (Shuster and Farley, 2004; Shuster et al., 2004). Regressions through these data are shown as dashed lines in the Arrhenius plots (Fig. 2), and the diffusion parameters extracted from each regression are indicated in Table 4 as the high retentivity domains (HRD). Sample 114 results were qualitatively duplicated in a more coarsely conducted experiment (not presented) on a different aliquot of smaller physical aggregate size. In that experiment, both the overall shape of the Arrhenius plot, and the regression through the HRD were in excellent agreement with the results presented in Figure 2.

Goethite 111.2, as defined by the array of lower diffusivities, is slightly more helium retentive than sample 114. As discussed below, the two arrays have the following diffusion parameters: $E_a^{114} = 162.8 \pm 2.4$ kJ/mol and $\ln(D_o/a^2) = 26 \pm 0.6$ ln(s$^{-1}$); and $E_a^{111.2} = 178.4 \pm 2.6$ kJ/mol and $\ln(D_o/a^2) = 28.3 \pm 0.6$ ln(s$^{-1}$), for samples 114 and 111.2, respectively. By assuming a diffusive length scale $"a"$ of 0.5 μm for both samples (Fig. 1b and see Discussion), we can estimate the frequency factors $D_o$ with which to compare these results to other phases commonly used for (U-Th)/He dating. We estimate the following values: $\ln(D_o) = 6.2$ and $\ln(D_o) = 8.5$ ln(cm$^2$/s), for samples 114 and 111.2, respectively. Durango apatite and FCT titanite each have comparable activation energies (148 and 183 kJ/mol, respectively), but lower frequency factors ($\sim 3.4$ and $\sim 4.1$ ln(cm$^2$/s), respectively; (Reiners and Farley, 1999; Farley, 2000)), indicating that the polycrystalline goethite is less helium retentive than these phases.

6.2. Radiogenic $^{4}$He Diffusion Coefficients

Shown in Figure 3, the diffusion coefficients calculated from $^{4}$He are initially lower than those calculated from $^{3}$He and are also significantly lower than the HRD linear regressions discussed above and shown in Figure 2. For instance, in the 114
experiment, the early step at 100°C yielded a value of $D/a^2$ that is a factor of $1.2 \times 10^{-4}$ lower than the HRD $^3$He based extrapolation. However, as each experiment proceeded toward higher gas yields, the apparent $ln(D/a^2)$ coefficients calculated from each isotope became gradually convergent. At the highest temperatures and latest steps of each experiment, the results calculated from $^3$He become statistically indistinguishable from $^4$He. These features are expected if proton-induced $^3$He and radiogenic $^4$He have equivalent diffusivity in goethite and the natural $^4$He has a diffusively modified spatial distribution (Shuster and Farley, 2004; Shuster et al., 2004).

6.3. Ratio Evolution Diagrams

A $^4$He/$^3$He ratio evolution diagram ($R_{step}/R_{bulk}$, where $R = ^4$He/$^3$He vs. cumulative $^3$He release fraction, $\Sigma F^3He$) is useful for constraining the spatial distribution of $^4$He in proton irradiated samples (Shuster and Farley, 2004). The measured ratio evolution diagrams for each experiment are shown in Figure 4. In each experiment, the values of $R_{step}/R_{bulk}$ are very low when $\Sigma F^3He < 0.1$ followed by a sharp and continuous increase to values that are more consistent with the bulk $^4$He/$^3$He ratio ($R_{step}/R_{bulk} \sim 1$). The increase to higher values of $R_{step}/R_{bulk}$ occurred more gradually for sample 114 than for sample 111.2. For instance, $R_{step}/R_{bulk}$ of sample 114 increased from $\sim 0$ to values $\geq 1.0$ in the range of $\Sigma F^3He$ from 0.04 to 0.30. The same occurred abruptly for sample 111.2 in the range of $\Sigma F^3He$ from 0.07 to 0.12. Note that the high density of values at $\Sigma F^3He \sim 0.15$ were determined during retrograde heating cycles in each experiment.

Once each of the stepped experiments evolved to $R_{step}/R_{bulk} \geq 1.0$, the measured ratios remained relatively constant. However, whereas the last few steps in the sample 114 experiment continually increased, the last few steps of sample 111.2 slightly but significantly decreased from a maximum value obtained when $\Sigma F^3He \sim 0.2$. Most of the information about a $^3$He distribution is expressed at low gas yields ($\Sigma F^3He < 0.4$) of a single domain ratio evolution diagram (Shuster and Farley, 2004). At low yields the effects of diffusive loss are most pronounced. For this reasons we focused on the $^4$He/$^3$He ratios when $\Sigma F^3He < 0.4$ to interpret Figure 4.

6.4. Helium Retentivity

Because supergene weathering products likely have isothermal histories (precipitation and residence at low temperatures), the closure temperature ($T_c$) is inappropriate for characterizing helium retentivity. Instead, we borrow a simple model of isothermal diffusive loss and radiogenic in-growth, presented by Ozisik (1989) and modified for He dating as presented in Wolf et al. (1998). For given functions of $D(T)/a^2$, plots of isothermal holding time ($t$) vs. expected He age ($t'$) can be calculated to evaluate the effect of diffusive $^4$He loss upon a He age.

In Figure 5 we present helium retention factors (curves plotted as He age/holding time ($t'/t$)) for three isothermal temperatures as functions of isothermal holding times. The calculations are shown for the HRD diffusivity functions $D(T)/a^2$ for the two samples. Note that here we discuss only the curves and that the points corresponding to “corrected ages” will be considered in a later section (see He age corrections). The curves in Figure 5 clearly illustrates that the helium retentivity of the two samples is different. For instance, at 25°C after 10 Myrs the HRD in sample 114 would have a deficit gas fraction of 10% (He age/holding time $\approx 0.90$), whereas the
HRD in sample 111.2 would have a deficit gas fraction of only ~1%. Deficit gas fractions are defined as \((N_{\text{uniform}} - N_0)/N_{\text{uniform}}\), where \(N_0\) is the total amount of \(^4\)He in a diffusively modified profile \((N_0)\) and a uniform profile \((N_{\text{uniform}})\) resulting from quantitative retention (Shuster and Farley, 2004).

The curves in Figure 5 also illustrate that helium retention in polycrystalline goethite is strongly temperature dependent. Future studies involving goethite will require careful sample selection and consideration of thermal conditions. For instance, these goethites would be susceptible to diffusive \(^3\)He loss associated with intense solar heating and episodic forest fires if they were located at the surface. The results clearly indicate that \(^3\)He is not expected to be quantitatively retained in the two Bahia samples, but that significant fractions of gas should be retained. Although the curves presented in Figure 5 are useful for predicting an expected degree of diffusive loss, a detailed interpretation of the ratio evolution diagrams should permit quantification of the deficit gas fraction.

### 7.STEPWISE DEGASSING EXPERIMENTS—DISCUSSION

Under the assumption that proton-induced \(^3\)He was uniformly produced and reflects all of the diffusion domains that may be present in each sample, the interpretation of the ratio evolution diagrams (Fig. 4) yields a quantitative description of the deficit gas fraction. In this sense, our treatment of the diffusion domains should permit prediction of an expected degree of diffusive loss, a detailed interpretation of the ratio evolution diagrams should permit quantification of the deficit gas fraction.

#### 7.1. Two-Domain Model

To describe the \(^3\)He release patterns for each experiment, we developed two-domain models to reproduce the observed \(^3\)He Arrhenius plots. Since the bulk of each sample (the HRD) was well characterized by the arrays of lower diffusion coefficients, a relatively narrow range in HRD diffusion parameters was permissible in the models. And, since the two arrays in each experiment were quite distinct, the volume fractions of the LRD were well approximated by the cumulative \(^3\)He release fraction up to the point the arrays converge (4 and 8% as discussed above). Therefore, the two-domain models each effectively had only two free parameters, \(E_a\) and \(ln(D_0/\alpha^2)\) for the LRD. However, diffusion coefficients calculated throughout the experiment are somewhat dependent upon the LRD, and the extraction of the HRD diffusion parameters from Figure 2 requires consideration of all domains present. Although more complicated models involving more than two domains or a continuum of domains could be developed, the highly simplified two-domain models are sufficient to explain the \(^3\)He observations. As such, we must emphasize that each two-domain model is a non-unique solution.

The models were calculated by assuming that the \(^3\)He distributions were initially uniform within two distinct populations of domains, and gas was not permitted to exchange between domains. Release fractions from the HRD and LRD were calculated separately using the heating schedules of each experiment, then summed at each step to yield a two-domain model \(^3\)He release pattern. The calculations were iterated by adjusting \(E_a\) and \(ln(D_0/\alpha^2)\) for the LRD until each model was consistent with the observed Arrhenius plots shown in Figure 2.

The best-fit two-domain models are shown in Figure 2 as solid curves. We found model parameters that successfully reproduce the shapes of the Arrhenius plots and that the activation energies of the LRD are well approximated by the slopes of the LRD arrays. We also found that the best-fit model diffusion parameters for the HRD were well approximated by the independent linear regressions through the arrays of lower diffusivity (see above). This is primarily due to the substantial difference in diffusivity between the two domains. For reference, the LRD and HRD diffusion parameters are plotted as dotted and dashed lines, respectively in Figure 2 and also summarized in Table 2.

Under the two-domain model, the \(^3\)He Arrhenius plots indicate that the helium diffusion in the LRD behaves quite differently between sample 114 and 111.2. Although both of the LRD are effectively non-helium-retentive over geologic time, their relative proportions are important characteristics of each sample. Although the diffusion properties of each LRD may provide insight into what the domains represent (see below), the excellent agreement between models and observations in
7.2. Quantifying Deficit Gas Fractions

If the spatial distribution of $^4$He within the goethites can be constrained, then the deficit gas fraction can be quantified. The deficit gas fraction is useful for correcting an absolute He age for diffusive $^4$He loss.

Given the two-domain models summarized in Table 2, and using the methods described by Shuster and Farley (2004), we simulated the expected $^4$He distributions within the samples under different isothermal conditions over geologic time. We assumed that the diffusivity of proton-induced $^3$He and radiogenic $^4$He is equivalent in these samples, although our results are not strongly sensitive to this assumption (Shuster et al., 2004). Each simulation was required to result in the observed He ages (10.7 and 42.6 Ma for sample 114 and 111.2, respectively), and each corresponds to a different deficit gas fraction.

The model $^4$He distributions were first calculated for the HRD of each sample, and then passed through a simulated degassing experiment to produce a set of $^4$He release fractions. Because the LRD of each sample is effectively non-retentive, their presence could be ignored in the profile calculating step. For instance, any radiogenic $^4$He produced within the LRD would be “immediately” lost on a geologic timescale. To simulate ratio evolution diagrams, a uniform distribution of $^3$He within both domains was also passed through the same simulated degassing experiment from which model $^4$He/$^3$He could be calculated.

The $^4$He modeling results are presented as curves in Figure 4. Several features in the models of both samples are immediately apparent. First, the models successfully reproduce the low $^4$He/$^3$He ratios at the beginning of each experiment. This is clearly controlled by the relative proportion of the $^4$He-only containing LRD and illustrates how well those proportions are constrained. Second, both sets of models successfully reproduce the gradual and sharp rises in $^4$He/$^3$He for sample 114 and 111.2, respectively, each followed by nearly invariant ratios.

Although the models do not perfectly match the data, we can use them to place strong limits on the degrees of diffusive $^4$He loss for each sample. For instance, if the models are accurate, sample 114 has retained >75% of its $^4$He, and 111.2 has retained >90%. We can also rule out the possibility that either sample quantitatively retained $^4$He. Despite significant scatter in the data, particularly during the retrograde cycles during which gas yields were low, we find that a 10% and a 2.5% deficit gas fraction best reproduces the results of sample 114 and 111.2, respectively.

7.3. He Age Corrections

Assuming that both domains are inherent to each sample and that radiogenic $^4$He was naturally produced uniformly throughout each domain, the modeling results suggest that two components must be quantified and added back into the $^4$He budget of each sample to correct its (U-Th)/He age. These components are the $^4$He quantitatively lost from the non-retentive LRD and the deficit gas fraction of $^4$He diffusively lost from the HRD of each sample.

Using a HRD deficit gas fraction of 10% for sample 114, we can correct the measured $^4$He concentration for partial diffusive loss from those domains, where corrected He content = measured content $\div (1 - \text{deficit gas fraction})$ (Shuster and Farley, 2004). This corrects the measured He age (10.7 Ma) to 11.8 Ma. The LRD represents 4% of the total $^3$He budget. If $^4$He produced in the LRD was quantitatively lost over geologic time, a similar correction brings the final corrected He age to 12.3 Ma. If we conservatively assume 100% uncertainty on each correction, the final age of sample 114 is 12.3 ± 1.6 Ma. For BAH-F124-111.2 we estimate the HRD deficit gas fraction to be ~2.5% and the fraction of gas lost from the LRD to be 8%. Applying both corrections and assuming 100% uncertainty on each brings the measured He age of 42.6 Ma to a final corrected age of 47.5 ± 4.9 Ma for sample 111.2.

It is difficult to estimate the actual uncertainty associated with the two corrections we describe above. Uncertainties associated with measured release fractions, linear Arrhenius regressions and the fits of $^4$He Arrhenius models, individual He, U and Th measurements, raw aliquot He age reproducibility, U series secular dis-equilibrium and the fits of ratio evolution models all contribute to the final uncertainty of a corrected He age. In these types of samples, we can easily measure [$^4$He], [U] and [Th] to better than ~1% analytical precision, and we find good He age reproducibility (Table 1). However, the uncertainty in a weathering product He age will be dominated by the uncertainty in He loss corrections described above. By assuming 100% uncertainty, we place a very conservative estimate of the uncertainty in a corrected He age.

An important caveat to the HRD correction is the possibility that an even higher retentivity domain exists in the sample but is not interrogated until the final total fusion of the sample at ~1300°C (last step, Table 3). Such a domain would be unrecognized in Figure 2. However, since a domain of sufficiently distinct retentivity would likely require distinct chemistry, the domain may have a different U, hence $^4$He content. Such a scenario could be recognized by the ratio evolution diagram if the total fusion step had a sufficiently different $^4$He/$^3$He than the rest of the sample. Rigorously, the HRD correction is only valid for the fraction of the sample interrogated by the Arrhenius plot. We have implicitly assumed that domains of higher retentivity than the HRD do not exist in either sample.

The magnitude of the above corrections illustrates the limitation of this dating technique and emphasizes the value of performing a stepped degassing analysis on a sample. Although more labor intensive than determining a basic (U-Th)/He age, the ability to recognize non-quantitative $^4$He retention and apply age corrections improves the accuracy of the precipitation ages.

7.4. Internal Consistency and Mean Temperature

If the corrected He ages represent the true precipitation age of each sample, the pair of Bahia goethites provides a test for internal consistency. Goethite samples 114 and 111.2 were located 3 m from one another in the weathering profile. For at least the duration of the younger sample’s existence, this pair must have shared a common thermal history. We a priori expect...
that mean temperatures these samples experienced was controlled by the mean annual air temperature of the region, 23°C. Although the mean temperature over the last ~40 Myrs is not well known, the samples should have remained well below 35°C throughout their existence.

Using 3He derived diffusion parameters for the HRD of each sample, the production/diffusion model predicts a He age and concentration profile for a given isotermal holding time and temperature (Fig. 5, curves). The diffusion-corrected He ages and the HRD deficit gas fractions determined from Figure 4 provide us the ability to superimpose each sample on the curves, shown as solid circles. Each sample indicates a physically reasonable residence temperature of ~25°C. The agreement between these results and the actual mean temperature of 23°C is significant, indicating that the diffusive loss corrections, the LRD corrections, and the temperature extrapolations of the 3He determined functions D(T)/a² are not severely inaccurate. Failure of this test would indicate inaccuracy in any of the above.

7.5. Physical Significance of Diffusion Domains

The physical significance of the apparent diffusion domains remains an unanswered question about these samples. Unlike single euhedral crystals, in fine grained polycrystalline material the physical identity of diffusion domains is unclear. The diffusion domain(s) may correspond to individual FeOOH crystals of various sizes, amorphous intergranular media, or even the bulk aggregate geometry in the case of the HRD.

If the bulk aggregate geometry defines the high retentivity diffusion domains, then we expect to find a difference between the two diffusion experiments performed on BAH-F124-114. Because we analyzed an aliquot ~1 mm in chip radius and one ~200 µm in radius, a difference in ln(D/a²) of ~3 natural log units would be expected. Although the aliquots were not perfectly spherical, a difference in ln(D/a²) of 3 ln units should be detectible despite the coarseness with which the 200 µm experiment was conducted. We found no significant difference between the HRD regressions of each Arrhenius plot. This implies that the characteristic domains size, a, is significantly smaller than the bulk aggregate geometry, and common to both aliquots.

The LRD diffusion parameters of sample 111.2 are very different from the rest of the sample, and also very different from the LRD of sample 114. Although both of the LRD diffuse helium rapidly, the very low activation energy (46 kJ/mol) of the LRD of sample 111.2 indicates those domains are fundamentally distinct from the rest of the sample. Previous work with Mn oxides revealed the residence of 40Ar in domains thought to be very low retentivity intergranular regions. This intergranular domain hosts atmospheric 36Ar, 38Ar, and 36Ar, but does not contain any significant radiogenic (36Ar*) or nucleogenic gas (e.g., 37Ar and 39Ar). The volume of intergranular space determines the density of the sample and depends on the packing of the acicular or rod-shaped hollandite and goethite micro-crystallites. In addition, the retentivity of the intergranular space may vary locally, depending on crystallite shape, size, and packing density. If this is also true of helium in polycrystalline goethite, we should expect variability in the relative proportions of HRD and LRD between samples related to the packing density of aggregated crystals and crystallinity index. Future studies involving careful characterization of sample crystallinity and trace chemical impurities are required to fully understand the physical significance of the apparent domains.

7.6. General Extrapolation of Goethite Diffusion Parameters

Despite general agreement between the measured diffusion parameters for the two goethites, every polycrystalline goethite aggregate may behave differently. The diffusion domain size distribution as well as an aggregate’s physical characteristics such as crystallinity and morphology may vary significantly from sample to sample. Until the relevant parameters that control 3He diffusion in goethite have been identified and quantified, it may be necessary to perform an irradiation/diffusion experiment to accurately interpret or correct goethite He ages.

8. CONCLUSIONS

Goethite (U-Th)/He dating is a viable weathering geochronometer. We found (U-Th)/He ages determined on aliquots of polycrystalline goethite to be reproducible despite variability in U and Th content. Stepwise degassing analyses of proton-irradiated aliquots have revealed the following about two polycrystalline goethites: (1) 3He does not reside in a single diffusion domain, but resides in at least two distinct domains; (2) two-domain models constrain the functions D(T)/a² for each domain and the relative proportions of 3He located in each; (3) ratio evolution diagrams reveal diffusive 3He distributions...
within the samples; and (4) the two samples retain $^4$He to different degrees.

Although $^4$He is not quantitatively retained in aggregated polycrystalline goethites, the magnitude of diffusive loss is not prohibitive. The ability to rigorously quantify diffusive-loss corrections by using the proton-irradiation $^4$He/$^4$He method enables goethite precipitation ages to be determined.

The widespread distribution of goethite in weathering profiles on Earth and possibly other terrestrial planets and the feasibility of dating goethite by the (U-Th)/He method opens new opportunities for quantifying water-rock interaction in the geological past. Application of goethite (U-Th)/He dating, if combined with stable isotope studies (O, H, and C), may provide a feasible mechanism for generating a nearly continuous paleoclimatic curve for continental areas suitable for comparison with the record preserved in oceanic reservoirs.

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