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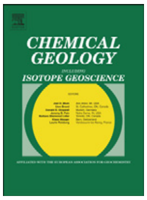

Applications and limitations of U–Th disequilibria systematics for determining ages of carbonate alteration minerals in peridotite

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ABSTRACT

^{238}U–^{234}U–^{230}Th dating was conducted on carbonate alteration minerals in the peridotite layer of the Samail Ophiolite, Sultanate of Oman, in order to assess the applicability of U-series dating techniques to these types of Quaternary terrestrial carbonates and also to further constrain natural rates of carbonation of the peridotite. Due to their low U concentrations and relatively high Th/U ratios, Samail carbonates are challenging to date with the ^{230}Th technique because of the sensitivity of ages to corrections for initial ^{230}Th. Uncorrected ^{230}Th ages for Ca-rich travertines are consistently older than previously obtained ^{14}C ages. However, geologically reasonable initial ^{230}Th corrections bring the two sets of ages into concordance. This age concordance suggests that the travertines are generally closed systems, adding a level of credence to the reliability of previously obtained ^{14}C ages. In contrast, uncorrected ^{230}Th ages for Mg-rich carbonate veins are generally younger than previously obtained ^{14}C ages. These young ages are interpreted in terms of remobilization of hexavalent U, which is subsequently deposited as tetravalent U by reduced serpentinization fluids. Two Mg-rich carbonate veins sampled at a roadcut have near-equilibrium (^{230}Th/^{238}U) and (^{234}U/^{238}U) values, which indicate that these veins are >375,000 years in age, consistent with their "^{14}C dead" (>50,000 years BP) ages. The variable young and old ages for these Mg-rich carbonate veins indicate that carbonation of the peridotite layer of the Samail Ophiolite is an ongoing process and that there have been multiple generations of subsurface carbonate vein formation. Overall, this study provides insights into some of the challenges associated with applying U-series dating methods to Quaternary terrestrial carbonates, in particular carbonate alteration minerals in peridotites, and highlights some areas where there is room for improvement, such as obtaining better constraints on the isotopic composition of admixed detritus, and also some advantages, such as the ability to identify open system behavior not apparent from ^{14}C dating and stable C and O isotopic analysis alone.

1. Introduction

Determining timescales of the formation and preservation of carbonate alteration minerals in mantle peridotite is essential in order to better understand the role of this potentially important sink in the global carbon cycle and also to evaluate the feasibility of using artificially enhanced, *in situ* formation of carbonates in peridotite as a method for mitigating the buildup of anthropogenic CO_2 emissions in the atmosphere (e.g. Seifritz, 1990; Lackner et al., 1995; Lackner, 2002; Kelemen and Matter, 2008; Matter and Kelemen, 2009; Kelemen et al., 2011). While natural carbonation of peridotite is commonly observed subaerially and on the seafloor (e.g. Trommsdorff and Evans, 1977; Trommsdorff et al., 1980; Ferry, 1995; Surour and Arafa, 1997; Kelley et al., 2001, 2005; Früh-Green et al., 2003; Ludwig et al., 2006, 2011; Kelemen and Matter, 2008; Matter and Kelemen, 2009; Power et al., 2009; Kelemen et al., 2011; Pronost et al., 2011; Beinlich and Austrheim, 2012; Harrison et al., 2013; Chavagnac et al., 2013a, 2013b; Mervine et al., 2014), the natural rate of peridotite carbonation and therefore the rate of CO_2 uptake via this alteration mechanism is poorly known (e.g. Wilson et al., 2006, 2009a, 2009b; Kelemen and Matter, 2008; Kelemen et al., 2011; Mervine et al., 2014). In part, this is because carbonate alteration minerals in peridotite are challenging to date. Several studies (e.g. Kelemen and Matter, 2008; Wilson et al., 2009b; Kelemen et al., 2011; Mervine et al., 2014) have employed ^{14}C dating, but this dating technique has a practical limit of only ~50,000 years. Use of the ^{238}U–^{234}U and ^{234}U–^{230}Th disequilibria dating techniques (which have practical dating

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limits of ~1 million years and ~375,000 years, respectively) and the U–Pb dating technique (which is suitable for dating on timescales of millions of years) to investigate longer timescales of carbonation is limited by the generally low (ppb level) U concentrations of peridotites and their associated carbonate alteration minerals (e.g. Hanhøj et al., 2010; Bodinier and Godard, 2014). Carbonates formed in peridotites at the Lost City Hydrothermal Field, which is located off-axis of the Mid-Atlantic Ridge, have been dated using U–Th disequilibria techniques (Ludwig et al., 2011). However, these carbonates have high U concentrations (ppm level) due to contribution of U from seawater (Ludwig et al., 2011). Historically, little work has been done to apply the U–Pb dating technique to carbonates although recently there has been some development in this field, with a focus on dating of speleothem samples with high U and low common Pb concentrations (e.g. Rasbury and Cole, 2009; Woodhead and Pickering, 2012; Hellstrom and Pickering, 2015).

Furthermore, while some carbonates, particularly corals and speleothems, are routinely dated with U–Th disequilibria methods (e.g. Edwards et al., 2003), dating of terrestrial carbonates with these techniques can be challenging due to the significant presence of admixed detritus. Unlike most corals and speleothems, terrestrial carbonates are usually affected by the presence of initial ^{230}Th and, to a lesser extent, by ^{234}U and ^{238}U contributed by detrital material (e.g. Bischoff and Fitzpatrick, 1991; Luo and Ku, 1991; Kaufman, 1993). This detritus is often fine-grained and intergrown with the carbonate, making physical separation very difficult (e.g. Ku and Liang, 1984; Bischoff and Fitzpatrick, 1991; Luo and Ku, 1991). Various approaches have been attempted over the years to account for detrital ^{230}Th, ^{234}U, and ^{238}U in terrestrial carbonates, including light acid leaching, separating the carbonate material from the admixed detritus, and pseudoisochron methods for determining the composition of incorporated detritus (e.g. Osmond et al., 1970; Schwarcz and Lathan, 1989; Przybylowicz et al., 1991; Bischoff and Fitzpatrick, 1991; Luo and Ku, 1991). However, these techniques have had limited success. In most cases, employing total sample dissolutions with corrections for detrital inputs is the most robust way to obtain U–Th disequilibria ages for terrestrial carbonates (e.g. Kaufman, 1993; Ludwig and Titterington, 1994; Edwards et al., 2003). However, terrestrial carbonates with low U concentrations and high Th/U ratios, such as carbonate alteration products formed in peridotites, can be challenging to date with U–Th disequilibria methods since the ages are highly sensitive to detrital corrections.

In this study we examined the applications and limitations of using U–Th disequilibria methods to date carbonate alteration minerals that formed in peridotites of the Samail Ophiolite, Sultanate of Oman (Fig. 1). The Samail Ophiolite is one of the largest and best-exposed ophiolites in the world (Glennie et al., 1973, 1974; Coleman, 1977, 1981; Lippard et al., 1986; Nicolas et al., 2000) and is thus an excellent location for investigating natural rates of carbonate formation in peridotite. The goal of this study was to determine ^{238}U–^{234}U and ^{234}U–^{230}Th ages and age limits for Samail carbonates in order to further assess the range of ages of carbonate alteration minerals in the peridotite layer of the Samail Ophiolite. This study builds upon previous ^{14}C dating and stable C and O isotope analyses of Samail carbonates, which are presented in Mervine et al. (2014) and also in Clark and Fontes (1990), Clark et al. (1992), Kelemen and Matter (2008), and Kelemen et al. (2011). Because these Quaternary terrestrial carbonates contain significant admixed fine-grained detritus, we undertook methods to: (1.) attempt to separate the aluminosilicate detritus from the carbonate or (2.) accurately correct for the effect the detritus is having on the ^{238}U–^{234}U–^{230}Th isotope systematics of the carbonate minerals. Comparing the ^{238}U–^{234}U and ^{234}U–^{230}Th ages and age limits determined for the Samail carbonates with previously published ^{14}C ages on the same samples (Mervine et al., 2014) enabled us to carefully scrutinize the reliability of ages obtained with both dating systems and to further constrain timescales of natural carbonation of Samail Ophiolite peridotites.

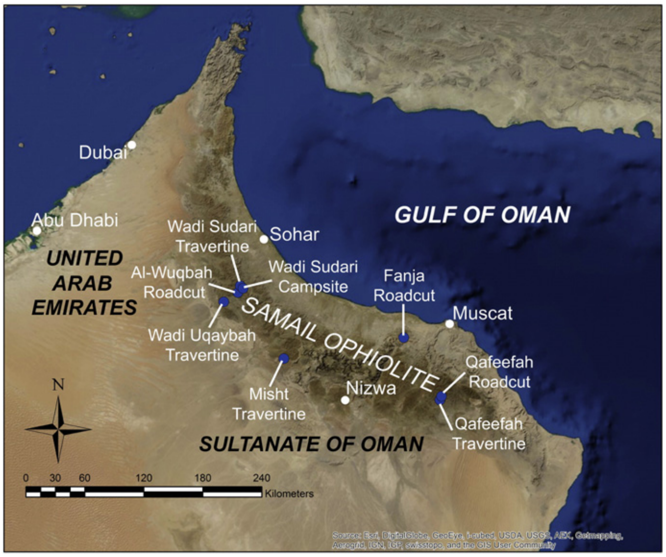

Fig. 1. The eight field locations (blue circles) where carbonate and peridotite samples were collected in the Samail Ophiolite during 2009 and 2010 field seasons. Map made using ArcGIS, Version 10.1.

2. Background

2.1. Terrestrial carbonates in the Samail Ophiolite

The Samail Ophiolite ranges from approximately 50 to 100 km in width and extends for greater than 500 km (e.g. Lippard et al., 1986; Nicolas et al., 2000). The ophiolite consists of several uplifted, thrust-bounded blocks (nappes) of oceanic crust and mantle that were obducted at ~80 to 95 Ma on top of autochthonous shelf carbonate rocks (the Hajar Supergroup) and parautochthonous continental slope carbonate rocks (the Sumeini Group), which rest on top of pre-Permian crystalline basement (Coleman, 1981; Lippard et al., 1986; Searle and Cox, 1999, 2002). These nappes consist of ~4 to 7 km of crustal rocks (layered gabbros, sheeted dikes, and volcanics, including pillow lavas) and ~8 to 12 km of upper mantle, primarily harzburgite (Glennie et al., 1973, 1974; Coleman, 1981; Lippard et al., 1986; Nicolas et al., 2000). Abundant carbonate veins as well as calcite-rich travertines are found throughout the peridotite layer of the ophiolite (e.g. Neal and Stanger, 1984, 1985; Clark and Fontes, 1990; Clark et al., 1992; Kelemen and Matter, 2008; Kelemen et al., 2011; Chavagnac et al., 2013a, 2013b; Mervine et al., 2014).

This study focuses on two types of carbonate alteration products that form in the peridotite layer of the Samail Ophiolite: (1.) travertine precipitated from high pH springs (Clark and Fontes, 1990; Clark et al., 1992; Kelemen and Matter, 2008; Kelemen et al., 2011; Paukert et al., 2012; Chavagnac et al., 2013a, 2013b; Mervine et al., 2014) and (2.) carbonate veins that form *in situ* in partially hydrated (serpentinized) peridotite (Matter and Kelemen, 2009; Kelemen et al., 2011; Streit et al., 2012; Mervine et al., 2014). These carbonates are thought to form as a result of low temperature alteration of peridotite through interaction with meteoric water (Fig. 2) (e.g. Barnes et al., 1967, 1978; Barnes and O'Neil, 1969, 1971; Neal and Stanger, 1985; Bruni et al., 2002; Cipolli et al., 2004; Kelemen et al., 2011). When meteoric water weathers partially serpentinized peridotite, Mg^{2+}–HCO_3^- rich waters (known as "Type I" waters) are formed. As these waters percolate deeper into peridotite bedrock where they are no longer in equilibrium with the atmosphere, they precipitate Mg-rich carbonates, serpentines, and clays. As a result of this precipitation and other reactions in the subsurface, the waters transform into Ca^{2+}–OH^- waters (known as "Type II" waters) that have very high pH (10 to 12) and low Mg, C, and oxygen fugacity (Eh approximately −200 mV) (Neal and Stanger, 1983, 1984, 1985; Clark and