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Early hydrothermal carbon uptake by the upper oceanic crust: Insight from *in situ* U-Pb dating

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ABSTRACT

It is widely thought that continental chemical weathering provides the key feedback that prevents large fluctuations in atmospheric CO_2, and hence surface temperature, on geological timescales. However, low temperature alteration of the upper oceanic crust in off-axis hydrothermal systems provides an alternative feedback mechanism. Testing the latter hypothesis requires understanding the timing of carbonate mineral formation within the oceanic crust. Here we report the first radiometric age determinations for calcite formed in the upper oceanic crust in eight locations globally via in situ U-Pb LA-ICP-MS analysis. Carbonate formation occurs soon after crustal accretion indicating that changes in global environmental conditions will be recorded in changing alteration characteristics of the upper oceanic crust. This adds support to the interpretation that large differences between the hydrothermal carbonate content of Late

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Mesozoic and Late Cenozoic oceanic crust record changes in global environmental conditions. In turn, this supports a model in which alteration of the upper oceanic crust in off-axis hydrothermal systems plays an important role in controlling ocean chemistry and the long-term carbon cycle.

INTRODUCTION

Earth's long-term carbon cycle requires a negative feedback mechanism such that increasing atmospheric CO_2 leads to increasing CO_2 drawdown into rocks (Berner and Caldeira, 1997). The standard model has this feedback principally driven by continental chemical weathering, largely through increased temperature and precipitation leading to increased riverine alkalinity fluxes to the ocean and hence greater carbon draw down (Berner, 2004). An alternative model suggests that the feedback is principally driven by increased alteration of the upper oceanic crust (lavas) in low-temperature (10's of Celcius), off-axis, hydrothermal systems (Brady and Gislason, 1997). This alternative model has found recent support based on: (i) the much higher C-content of ocean crust altered in the greenhouse climate of the Late Mesozoic than the icehouse climate of the Late Cenozoic (Gillis and Coogan, 2011); (ii) modeling of the seawater Sr-isotope curve that suggests that much of the rise in $^{87}Sr/^{86}Sr$ in the Late Cenozoic is due to decreasing ocean temperature leading to less unradiogenic Sr being leached from the upper oceanic crust (Coogan and Dosso, 2015); and (iii) modeling of the variability of seawater Mg-isotopes that suggests that the Late Cenozoic increase in Mg/Ca is due to cooling seawater leading to a reduced Mg sink into marine clays (Higgins and Schrag, 2015).

A key to testing the oceanic crust feedback model is understanding the duration over which a section of oceanic crust continues to chemically interact with the ocean. In

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detail this must depend on many local factors such as crustal permeability structure, sedimentation rate and seafloor topography. However, the global average duration of large-scale chemical exchange is the important factor in global geochemical cycles. For example, if alteration occurs soon after crustal accretion and then largely stops, the age of the crust can be used to estimate the global environmental conditions during alteration and hence test predictions of this model. In contrast, if the oceanic crust continues to chemically interact with the ocean over its entire lifetime, with little change in the rate of chemical exchange, then environmental conditions over the entire lifetime of piece of crust would have to be integrated into a model of the style of crustal alteration.

While previous studies have addressed the question of the timing of crustal alteration (see below) here we present a novel approach to radiometrically date secondary carbonate minerals for the first time. Carbonate (largely calcite except in very young oceanic crust which contains abundant aragonite) is a key phase because: (i) its age records the time of alkalinity generating reactions within the crust (Coogan and Gillis, 2013); (ii) based on textural relationships (i.e. relative ages) void filling carbonate has been proposed to record the final stage of upper crust alteration in any given sample (Staudigel et al., 1981; Alt and Honnorez, 1984; Gillis and Robinson, 1990); and (iii) its composition has been used to track changes in ocean chemistry (Coggon et al., 2010; Rausch et al., 2013) which is dependent on the assumption that carbonate forms soon after crustal accretion.

Sample Suite

Twelve samples were selected from eight different Deep Sea Drilling Project (DSDP) sites and two from the Troodos ophiolite to represent a range of crustal ages (81–

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148 Myr) and ocean basins (Table 1 and Supplementary Information[1]). Only relatively old locations were selected with the aim of determining how long after crustal accretion carbonate continues to form for. The samples are all from veins or, in one case, a feature that could be a vein or a vug, and are from the upper 100 m of the lavas. Sample sites were selected based on previous work having shown that alteration occurred at typical low temperatures; this is confirmed by O-isotope data that indicate formation temperatures between 9 and 23 °C similar to Cretaceous bottom water (Table 1). The rationale for this was that this would lead to the largest probability that the carbonates grew from typical seawater-like fluids, with high U and low Pb, giving the greatest possibility of carbonate materials with high U/Pb. Of the fourteen samples, three have extremely low U contents and low U/Pb making them impossible to date. These samples are not discussed further although the reader should keep in mind it is possible that the conclusions drawn below are only relevant to the 80% of carbonates dated.

ANALYTICAL TECHNIQUES

Chips of optically clean carbonate a few millimeters in size were mounted in epoxy for analysis. Measurements were analogous to LA-ICP-MS methods used for zircon U-Pb dating by Mottram et al. (2014) and carbonate U-Pb dating by Li et al. (2014) with normalization for U-Pb and $^{207}Pb/^{206}Pb$ using the 254 Myr old WC-1 calcite and NIST 614 glass, respectively. Multiple spots on a single grain were analyzed and the data regressed on Tera-Wasserburg plots using Isoplot to determine the sample age (Fig. 1). An in-house method was used for correction of inherent variability in the proportion of common lead in the WC-1 calcite. The Supplemental material[1] contains more detail on methods and full data tables. Uranium contents of samples were measured by

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normalizing the signal against that of the WC-1 calcite with an assumed ~5 ppm U content, and are therefore approximate. Uncertainties of ages reflect all analytical uncertainties and the uncertainty of the external standard used for normalization. Hand-picked optically clean carbonate from the same samples was analyzed for O-isotopic composition following the methods described in Gillis and Coogan (2011; Table 1).

RESULTS

Out of the eleven samples dated, the five most precise U-Pb ages (Fig. 1; Table 1) are for samples from DSDP Sites 417D, 418A and 543A in the western Atlantic and Site 163 in the equatorial central Pacific. These samples have 2σ precisions of better than ± 5 Myr (ages between 82 and 128 Myr). The three samples from Sites 417D and 418A, drilled within 10 km of one another, contain the highest U contents of any studied here with maximum U contents ranging from 0.5 to 10 ppm (Supplementary data). The samples from Sites 543A and 163 contain much lower U contents (maximum U contents of 80 and 120 ppb respectively) but still have some areas with relative high U/Pb allowing reasonably high precision age determinations. The data for the two samples with the highest U contents show some scatter (MSWD 4.8 and 5.3; Table 1), suggesting that other factors (multiple periods of growth, variable common lead isotope composition) could be important; the uncertainties take account of the scatter in regressions but their absolute uncertainties need to be used with some caution. Three samples have intermediate age uncertainties of ± 5–10 Myr (Fig. 1). These samples have maximum U contents ranging from 50 to 80 ppb but Pb contents generally <5 ppb allowing reasonably precise ages. The three samples with the largest uncertainties (±10–20 Myr) are from DSDP Site 595B (two samples) and the Troodos ophiolite; these samples contain <40

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ppb U. For all of these samples there are no analyses with low common lead and hence there is a large extrapolation from the array of data to the concordia age intercept and the uncertainties quoted should be considered as minimum values.

The new carbonate formation ages (Fig. 1; Table 1) provide the first direct determination of whether carbonate formation occurs soon after crustal accretion or throughout the life of a section of oceanic crust – both of which have been previously suggested (Staudigel and Hart, 1985; Alt and Teagle, 1999; Gillis and Coogan, 2011; Coogan and Dosso, 2015). Despite the analytical challenges in dating these materials it is clear that most carbonate forms soon after crustal accretion (Fig. 2); this interpretation is consistent with other preliminary data, collected in the same way, recently reported by Harris et al. (2014). Notably, none of the carbonate ages are >20 Myr younger than the crust despite all the study areas being in >80 Myr old crust. While fluid and heat fluxes are not expected to directly match chemical fluxes, it is notable that >80% of the off-axis hydrothermal heat flux is removed within 20 Myr of crustal accretion.

DISCUSSION

Conditions in the Aquifer During Carbonate Growth

Carbonate mineral precipitation in the upper oceanic crust occurs largely in response to fluid-rock reactions that generate alkalinity and hence increase the saturation state of carbonate minerals (Coogan and Gillis, 2013). Heterogeneity in the U and Pb contents of the carbonates (Fig. 1; Supplementary material[1]) suggests that the concentrations of U and Pb in the aquifer fluid, and/or environmental conditions (pH, redox, T), varied during carbonate growth. Formation of secondary minerals at low temperatures adds U to the crust (e.g., Staudigel et al., 1995) and will lead to decreasing

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U contents of the aquifer fluid as fluid-rock reaction progresses, at least partial explaining the observed variability in U/Pb. This fluid-rock reaction occurs despite the low carbonate formation temperatures (9–23 °C; Table 1). Such modification of the fluid composition, on timescales shorter than that of the growth of a single carbonate vein, needs careful consideration when interpreting past compositions of seawater from the compositions of carbonate minerals precipitated within the oceanic crust (e.g., Coggon et al., 2010; Rausch et al., 2013).

Modern deep seawater contains very little Pb (~2 ppt; Bruland et al., 2014) and has a high U/Pb (~1000) and fluids entering the crustal aquifer have probably had similarly high U/Pb throughout the Phanerozoic. The low Pb content of seawater, and its short residence time, means that the Pb-isotopic composition of seawater can vary on short timescales (kyr). Thus, variations in the Pb content, and isotopic composition, of the aquifer fluid during the growth of a carbonate vein may be caused by either: (i) changing seawater Pb content/isotopic composition, and/or (ii) fluid-lava or fluid-sediment reactions; i.e., no additional source of Pb is required by the Pb-isotope variability although it cannot be ruled out.

The excess scatter of the data about a linear correlation (i.e., MSWD >2.0 at 2σ) between $^{238}U/^{206}Pb$ and $^{207}Pb/^{206}Pb$ in some samples (Fig. 1) most likely reflects either: (i) varying Pb-isotopic composition of the fluid that the carbonate grew from, (ii) protracted carbonate growth and/or (iii) analytical factors difficult to correct for in low-signal analyses. Protracted growth of carbonates, perhaps over millions of years, may be a natural consequence of the large fluid fluxes required to supply sufficient C to the crust to form the mass of carbonate observed in some drill cores (Coogan and Gillis, 2013).

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Low-Temperature Alteration Occurs Early

It is clear from the new data reported here that most carbonate precipitation within the upper oceanic crust occurs within the first 20 Myr after crustal formation (>80%; Figure 2, 3). Our samples come from a wide range of locations and from crust with ages between 80 and 148 Myr but none of the carbonates ages are >16 Myr younger than the crustal age. The only previous approach to determining the timing of carbonate formation in the ocean crust compares the Sr-isotopic compositions of carbonates with the seawater Sr-isotope curve. This approach gives a non-unique result both because the seawater curve shows fluctuations in $^{87}Sr/^{86}Sr$, and because basalt dissolution lowers the $^{87}Sr/^{86}Sr$ of crustal fluids. Early qualitative approaches concluded that carbonates were precipitated within 10–15 Myr of crustal accretion assuming no basaltic Sr in the fluid (Staudigel and Hart, 1985). More recent quantitative models show that the data can be explained with an exponentially decreasing rate of carbonate precipitation with 85% of carbonate precipitated within <20 Myr of crustal accretion (Gillis and Coogan, 2011; Coogan and Dosso, 2015). The good agreement between the model ages and the direct age determinations presented here (Fig. 3) suggest that the assumptions inherent in the Sr-isotope model ages are reasonable.

It is useful to compare the U-Pb age distribution of carbonates with previous radiometric age determinations for other low temperature alteration minerals formed in the upper ocean crust. The most robust data sets come from K-Ar and Rb-Sr dating of celadonite with just a few alteration age determinations from Rb-Sr isochron ages that include clays and zeolites. Existing K-Ar ages of alteration of upper ocean crust come almost entirely from celadonites in the Troodos ophiolite (54 samples from Gallahan and

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Duncan, 1994, and 4 from Staudigel et al., 1986). Comparison of these K-Ar ages to Rb-Sr ages of 18 of the same celadonites suggests that they may have suffered some Ar-loss, with Rb-Sr dates generally older (by a maximum of 14 Myr and an average of 5 Myr; Booij et al., 1995). Celadonite formation as a function of time after crustal accretion follows a similar pattern to carbonate formation although perhaps offset toward forming slightly later (Fig. 3); this probably simply reflects different sample suites rather than a real difference in the timing of carbonate and celadonite formation. Likewise, the limited existing isochron age determinations of ocean crust alteration suggest this occurs soon after crustal accretion (e.g., Richardson et al., 1980; Staudigel et al., 1986). Thus it seems clear that, in general, the vast majority of the low temperature alteration of the upper oceanic crust occurs within 20 Myr of crustal accretion (Fig. 3).

Several studies have suggested that carbonates are the last phases to form during off-axis alteration of the upper oceanic crust (Staudigel et al., 1981; Alt and Honnorez, 1984; Gillis and Robinson, 1990). This is difficult to reconcile with the need for alkalinity generating fluid-rock reaction to drive carbonate precipitation because these must be accompanied by the formation of secondary silicates. The new age data suggest carbonates and secondary silicates form over the same time interval (largely in the first 20 Myr after crustal accretion) resolving this paradox.

Implications for the Regulation of Ocean Chemistry

The relatively rapid alteration of new upper oceanic crust (Fig. 2, 3) has important implications for testing whether low-temperature alteration of the oceanic crust plays an important role in the feedback mechanisms that regulate ocean chemistry and the long-term carbon cycle. If this model is correct then, on a timescale of 10–20 million years

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(i.e. the timescale of the majority of chemical exchange), there should be a correlation between the composition of altered oceanic crust and the global environmental conditions. The higher C content of Cretaceous than Cenozoic altered upper oceanic crust supports a model of increased alkalinity production during periods of globally warm conditions (Gillis and Coogan, 2011). This model also makes predictions for the average change in Sr and Mg isotopic composition of upper ocean crust of different ages (Coogan and Dosso, 2015; Higgins and Schrag, 2015), as well as other element and isotope systems. However, we caution that local crustal hydrological conditions will have to be considered to ensure a signal relevant to global fluxes is extracted from such data.

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FIGURE CAPTIONS

Figure 1. Tera-Wasserburg concordia plots showing $^{238}U/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ (age and uncertainty are show in the title). The samples are ordered such that the more precise ages are in the upper row and the least precise ages in the lower row.

Figure 2. Comparison of the measured carbonated age and the estimated age of the crust the carbonate came from. Considering the errors associated with both ages, the carbonate and crustal ages are virtually identical (gray symbols are samples shown in the lower row in Fig. 1, with large extrapolations to the age intercept). The inset shows the same but with the axes starting at zero, the time of sampling, showing more clearly that although the carbonates could, theoretically, have formed at any time after crustal accretion (i.e.,

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vertically down from the 1:1 line in the gray polygon) they actually formed very soon after crustal accretion.

Figure 3. Comparison of the cumulative fraction of secondary minerals formed by low temperature alteration of the upper oceanic crust as a function of time after crustal accretion based on carbonate U-Pb ages (this study), celadonite K-Ar ages (Gallahan and Duncan, 1994; Staudigel et al., 1986), celadonite Rb-Sr ages (Booij et al., 1995) and carbonate Sr-isotopic composition modeling (Coogan and Dosso, 2015). The probability distribution for each age determination was summed across all samples, accounting for the individual age uncertainties, and the positive portion of this used to calculate the cumulative frequency. In cases where the measured age distribution includes time before crustal accretion these were normalized out of the probability distribution; this is only of any significance for the U-Pb carbonate ages.

[1]GSA Data Repository item 2015xxx, [this provides further background on the sample sites and analytical techniques as well as all the full dataset], is available online at www.geosociety.org/pubs/ft2009.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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DOI:10.1130/G37212.1

TABLE 1: CARBONATE COMPOSITIONS AND AGES

Sample	Texture	Crustal age (Myr)	Ave U (ppb)	Ave Pb (ppb)	Age	MSWD	$^{207}Pb/^{206}Pb_{(i)}$	$\delta^{13}C$ (VPDB)[b]	$\delta^{18}O$ (SMOW)[b]	Formation temp. (°C)
595B-2R1–84–95*	vein	95	13	3.5	115 ± 16	1.5	0.87 ± 0.01	2.6	30.5	14.0
595B-3R2–12–18*	vein	95	19	2.1	86 ± 14	6.6	0.85 ± 0.02	2.4	30.2	15.0
543–16R6–114.5–118*	vug/vein	80.8	50	3.7	91.3 ± 4.9	1.5	0.87 ± 0.01	2.5	30.9	12.5
543–16R6–114.5–118D	vug/vein	80.8						3.0	30.9	12.3
163–29R5–0	vein	80.8	91	9.1	81.5 ± 3.3	1.15	0.85 ± 0.01	2.9	31.9	8.7
164–28R3–23	vein	109	32	1.8	117.6 ± 9.6	0.42	0.83 ± 0.03	2.7	29.9	16.6
164–28R4–44	vein	109	33	4.9	115.6 ± 5.4	1.07	0.84 ± 0.01	1.7	28.5	22.4
417D-27R4–61	vein	120	124	3.6	103.9 ± 3.1	0.31	0.83 ± 0.01	1.8	30.2	15.4
417D-31R4–8	vein	120	2457	49	127.5 ± 4.7	5.3	0.86 ± 0.05	1.6	28.4	22.9
418A-15R3–144	vein	119.9	534	18	121.9 ± 4.7	4.8	0.85 ± 0.03	2.5	29.1	19.8
307 13R2 145	vein	148.3	63	2.4	142.8 ± 8.6	0.9	0.83 ± 0.03	1.1	29.4	18.4
2012CL26	vein	91.6	19	4.4	105 ± 19	1.7	0.89 ± 0.02	1.5	31.9	8.5
2012CL26D	vein	91.6						1.5	31.9	8.5

Note: We arbitrarily assign a ± 2 Myr uncertainty to all crustal ages except DSDP Site 595 for which the uncertainty is clearly larger and we assign ± 10 Myr (Supplementary material). D - duplicate analysis. Formation temperatures are calculated assuming a fluid $\delta^{18}O$ of −1 per mil and using the thermometer of Epstein et al. (1953)

i—intercept

*O and C isotopes data from Gillis and Coogan (2011).

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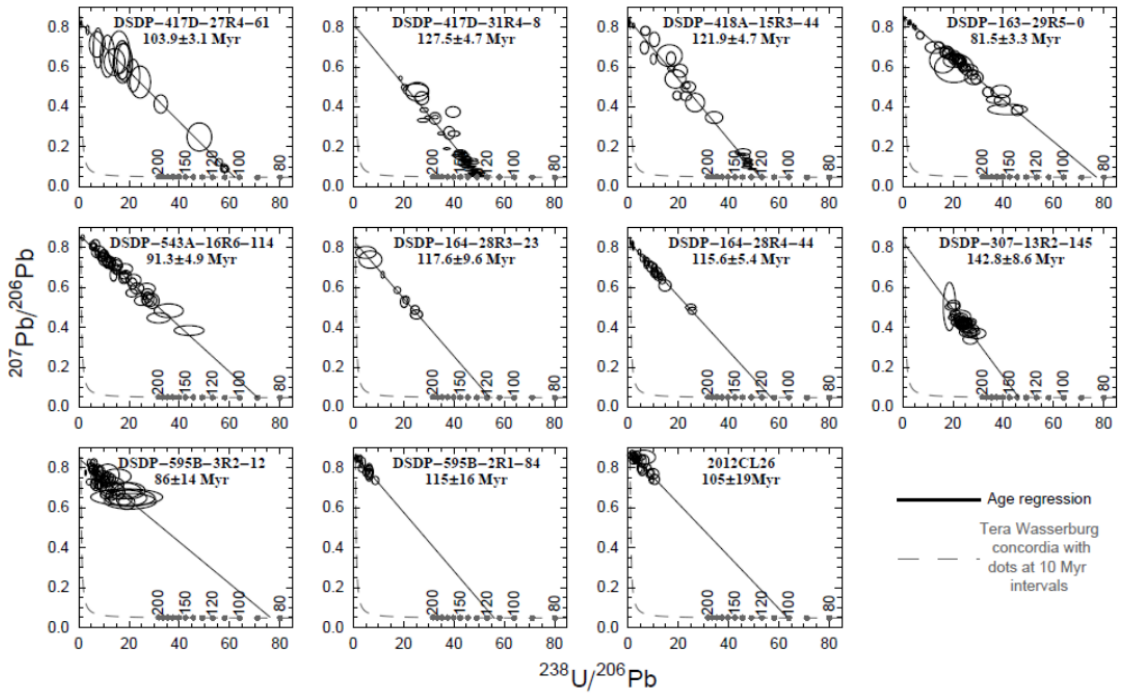
Journal: GEOL: Geology
DOI:10.1130/G37212.1

360 Figure1:



361
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363 Figure2:

Figure

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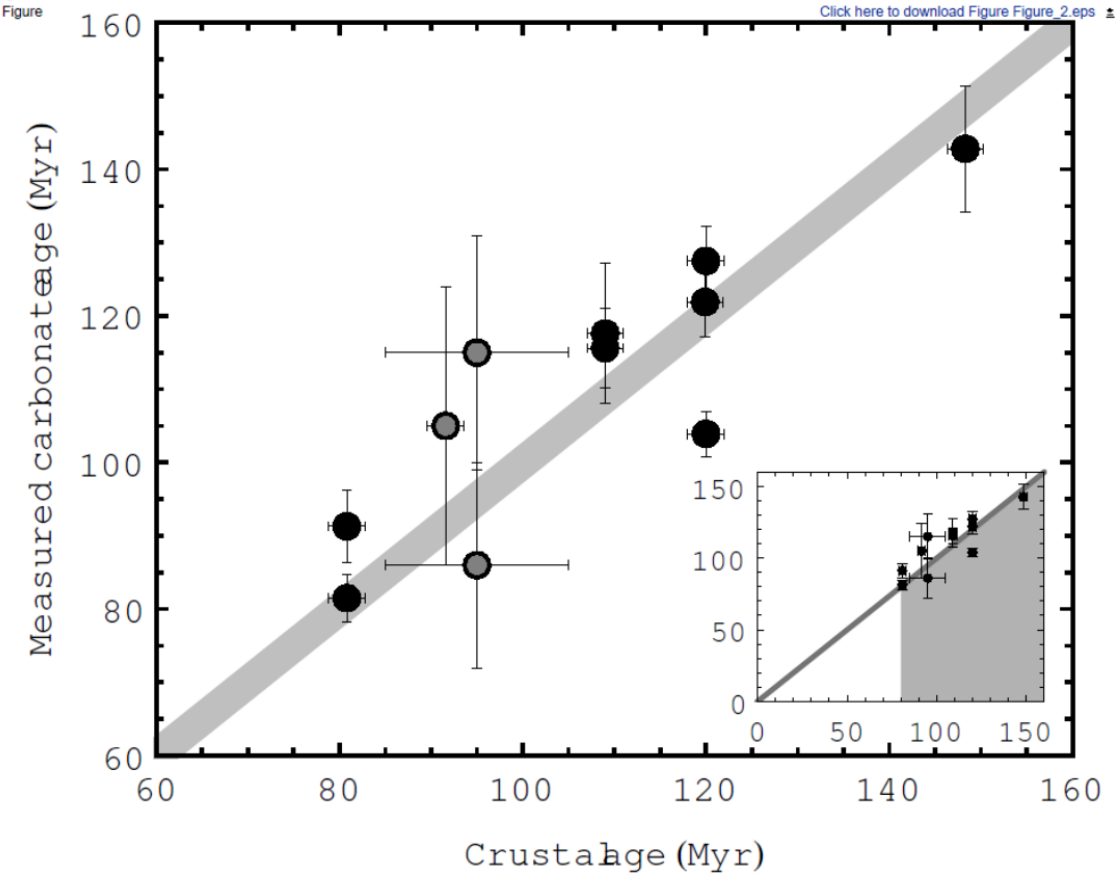

364

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Journal: GEOL: Geology
DOI:10.1130/G37212.1

Figure 3:
Figure 3