

**ACCELERATOR MASS SPECTROMETER  $^{14}\text{C}$  DETERMINATION IN  $\text{CO}_2$  PRODUCED  
FROM LASER DECOMPOSITION OF ARAGONITE**

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## ACCELERATOR MASS SPECTROMETER $^{14}\text{C}$ DETERMINATION IN $\text{CO}_2$ PRODUCED FROM LASER DECOMPOSITION OF ARAGONITE

### *Abstract*

Determination of  $^{14}\text{C}$  in aragonite ( $\text{CaCO}_3$ ) decomposed thermally to  $\text{CO}_2$  using an yttrium-aluminum-garnet doped neodymium laser is reported. Laser decomposition accelerator mass spectrometer (LD-AMS) measurements reproduce AMS determinations of  $^{14}\text{C}$  from conventional reaction of aragonite with concentrated phosphoric acid. The lack of significant differences between these sets of measurements indicate that LD-AMS radiocarbon dating can overcome the significant fractionation that has been observed during stable isotope (C and O) laser decomposition analysis of different carbonate minerals. The laser regularly converted nearly 30% of material removed to  $\text{CO}_2$  despite being optimized for ablation, where laser energy breaks material apart rather than chemically altering it. These results illustrate promise for using laser decomposition on the front-end of AMS systems that directly measure  $\text{CO}_2$  gas. The feasibility of such measurements depends on 1. the improvement of material removal and/or  $\text{CO}_2$  generation efficiency of the laser decomposition system and 2. the ionization efficiency of AMS systems measuring continuously flowing  $\text{CO}_2$ .

## *Introduction*

Determination of  $^{14}\text{C}$  content in carbon-bearing materials by accelerator mass spectrometer has significantly advanced fundamental debates involved chronology and carbon cycling. Intact carbon-bearing materials, such as accretionary aragonite (fish otoliths, sclerosponges, corals, etc.) and cellulose (hardwoods), have proven especially useful in assessing questions of ocean circulation, larval dispersion, and  $^{14}\text{C}$  production and variability. In cases where high spatial resolution is desired or where accretion rates are low, radiocarbon analysis is limited by the need for large samples. Sample size ultimately dictates analytical precision which is correlated to the total counts of  $^{14}\text{C}$  in the accelerator mass spectrometer (AMS) detector. Generally, sample sizes are targeted that minimize counting uncertainty and this targeted size differs depending on AMS source efficiency and spectrometer performance. In cases where ample carbon is available for optimal counting statistics, sample preparation (graphitization) is the main source of uncertainty in  $^{14}\text{C}$  determination.

The current vanguard of AMS  $^{14}\text{C}$  analysis is the development of ionization sources capable of ionizing  $\text{CO}_2$  gas for analysis rather than conventional graphite cathodes<sup>[1]</sup>. The potential benefits of such techniques lie in rapid analysis and minimization of graphitization-born uncertainty. This comes with a cost in reduced ionization efficiency<sup>[1]</sup>, but measurement of  $^{14}\text{C}$  in flowing  $\text{CO}_2$  has the potential to create new hybrid  $^{14}\text{C}$  analytical techniques. Such techniques would involve analytical instruments transporting carbon in a flow of gases or combustible liquids (e.g. gas chromatographs, liquid chromatographs, etc.) which can push their effluent directly through an oxidative furnace and into an ionization chamber for  $^{14}\text{C}$  monitoring of the flowing  $\text{CO}_2$ <sup>[1]</sup>. Laser micro-sampling devices also hold potential to ultimately be hybridized with gas-accepting AMS because of their suitability in analyzing intact carbon-bearing materials at high precision. In the geosciences, such laser systems have been widely used to ablate material into a colloidal suspension of fine particles in a flowing gas for various analyses<sup>[2-6]</sup>. The energy from laser sampling devices also heats surfaces which they contact in addition to ablating the surface; thus simultaneous chemical reaction and/or decomposition is expected. As a result, similar types of lasers (neodymium-doped yttrium aluminum garnet, or Nd-YAG) have been used on similar types of substrates (calcium carbonate) to analyze both ablated particles with inductively coupled plasma mass spectrometer (ICP-MS)<sup>[2, 4, 7]</sup> and evolved  $\text{CO}_2$  (from decomposition of  $\text{CaCO}_3$  (s) to  $\text{CaO}$  (s) and  $\text{CO}_2$  (g)) gas via gas-sourced isotope ratio mass spectrometer<sup>[3, 8-11]</sup>.

Here, we assess the potential for directly analyzing  $\text{CO}_2$  generated by a laser micro-sampling device for radiocarbon content by gas-accepting AMS. To

accomplish this, we address two main questions. First, the efficiency of a standard laser system is assessed in terms of the proportion of CO<sub>2</sub> generated to the amount of material removed. This question is imperative to <sup>14</sup>C determination because sample size requirements for radiocarbon content determination are much larger than those for stable isotope analysis. Second, the effects of carbon isotope fractionation in CO<sub>2</sub> generated by a laser micro-sampling system are assessed by comparing δ<sup>13</sup>C and Δ<sup>14</sup>C determinations between laser-generated CO<sub>2</sub> and conventional acid-generated CO<sub>2</sub> from the same sample of intact sclerosponge aragonite. The experiments and results described below indicate success in measuring reproducible Δ<sup>14</sup>C values using laser decomposition in a Nd-YAG micro-sampling system (Merchantek UP213) designed to operate at a frequency of 213 nm.

### *Methods*

**Laser system** - All tests were performed on intact calcium carbonate heated and ablated by a quintupoled Nd-YAG 213 nm wavelength laser microsampling system. The laser system (Merchantek UP213) is commonly used on the periphery of ICP-MS systems and is optimized for ablation of various materials. Previous work has determined this type of laser only minimally suitable for isotope measurements due to its low efficiency in generating CO<sub>2</sub> from optically clear materials such as calcite<sup>[3]</sup>. Thus, all tests described herein reflect less than optimal conditions and any success can be interpreted as expandable through the use of different, more efficient lasers. Despite the exclusive use of intact solid aragonite in this experiment, different materials (such as cellulose) may warrant use of different types of lasers to maximize CO<sub>2</sub> yield per unit material removed (hereunto referred to as “CO<sub>2</sub> efficiency”).

**Efficiency tests** – The efficiency of the 213 nm laser micro-sampling device in producing CO<sub>2</sub> was determined from the volume of material removed and the amount of CO<sub>2</sub> generated by boreholes drilled into the aragonite by the laser (Figure 1). The volume of the boreholes was determined by analysis both under the microscope of the laser system and an external microscope and compared to sample thickness. To determine the amount of CO<sub>2</sub> evolved, the laser chamber was flushed with UHP He gas flowing at 60 mL·min<sup>-1</sup> through a non-dispersive CO<sub>2</sub> detector. This flow represents approximately an order of magnitude less flow than that used to flush ablated products into the ICP-MS. The reason for low flow was to maximize sensitivity of the CO<sub>2</sub> analyzer (Figure 2); high flow used for transporting particles was not necessary to purge CO<sub>2</sub> gas from the laser chamber and low flow provided for a longer residence time in the optical cell of the CO<sub>2</sub> detector for better quantification. Concentrations of CO<sub>2</sub> were recorded in real time and integrated post-run to calculate the total amount

of CO<sub>2</sub> evolved by a single borehole. Calculations of efficiency assumed solid aragonite with a density of 2.9 g · cm<sup>-3</sup> [12]. Determinations were also made from laser holes in Icelandic spar (calcite) and fish otoliths (aragonite).

**Fractionation tests** – In order to demonstrate immunity of Δ<sup>14</sup>C to established isotope fractionation at the site of laser heating<sup>[3]</sup>, a single thick section of aragonite from a sclerosponge was measured both conventionally and by laser. Conventional analysis was performed with several aliquots of 1-10 mg of powdered sample removed by hand-held dental drill from the intact sclerosponge skeleton. The powder samples were evacuated and reacted with 100% H<sub>3</sub>PO<sub>4</sub> for 24 hours at 30°C. Equilibrated CO<sub>2</sub> gas was transferred and converted to graphite using iron-hydrogen reduction at 525°C (90% of the gas) and measured by isotope ratio mass spectrometer for δ<sup>13</sup>C relative to PDB (10% of the gas). In the AMS system, the graphite-iron mixture was sputtered with Cs<sup>2+</sup> in the ionization chamber for production of a C<sup>-</sup> ion beam which was converted to a C<sup>+</sup> beam after acceleration through diffuse argon to remove electrons as well as hydrides, and analyzed for <sup>14</sup>C/<sup>12</sup>C ratios.

Laser decomposition CO<sub>2</sub> was produced similarly to the efficiency tests. Raster patterns of slowly-scanned lines 100μm in width and 100μm in spacing were followed by the computer controlled laser. These raster patterns followed closely the skeletal banding present in sclerosponges. Raster pattern widths were either 2 or 5 mm perpendicular to the growth axis and 0.5 mm along the growth axis (Figure 1). The smaller sample widths (Figure 1, top) necessitated deeper penetration by the laser to generate enough CO<sub>2</sub>. The laser was operated at full power (approximately 20-25 J/cm<sup>2</sup>) with a pulse frequency of 20 Hz. Each pattern was repeated, with CO<sub>2</sub> from each trace ultimately integrated into one gas sample. Sample dimensions and distances from oral surface were verified with calipers. Laser-generated CO<sub>2</sub> was carried from the laser chamber by UHP He at 60 mL·min<sup>-1</sup>. Prior to photometric quantification with the CO<sub>2</sub> analyzer, the gases from the laser chamber were passed through a confluence with a low flow of UHP O<sub>2</sub> over an oxidized copper wire catalyst, upstream of two tube furnaces heated to 800°C (Figure 2). The goal of this step was to combust any CO from the incomplete decomposition of aragonite that has been reported from previous work using Nd-YAG lasers in the primary mode (1066 nm)<sup>[3]</sup>. Flow rates of ultra-high purity He carrier gas were identical to those in the efficiency test method. The gas mixture flowed into a two-trap, six-valve assembly designed to switch between flow at atmospheric pressure and vacuum. Liquid nitrogen was used to immobilize the CO<sub>2</sub> in the flow-through trap for transition to the vacuum line. Subsequent to full integration of a single sample with the trap, CO<sub>2</sub> was transported passively into a vacuum line and separated from water and other gases and then sealed into an evacuated Pyrex tube for analysis. Gas samples

were treated identically to CO<sub>2</sub> produced by conventional acid digestion of aragonite, except cobalt was added to convert the gas to graphite because samples were below 7 μmol carbon.

**Radiocarbon analysis** – All radiocarbon measurements were made on the National Ocean Sciences AMS (NOSAMS) system at Woods Hole Oceanographic Institution. Isotope ratios were calculated relative to a laboratory oxalic acid standard. Stable isotope ratios were also measured with the AMS system, in addition to external isotope ratio mass spectrometer (ir-MS) measurements.

### *Results*

Efficiency tests were run until CO<sub>2</sub> production from a single borehole returned to baseline conditions (Figure 3). Release of CO<sub>2</sub> was not measureable when the epoxy resin used to attach calcium carbonate samples to glass slides was heated by the laser during the short durations of individual efficiency tests. At low flow rates, noise in the CO<sub>2</sub> quantification was small compared to the signal of a typical borehole (Figure 3). Efficiency was calculated by

$$\varepsilon_{CO_2} = \frac{100 \cdot mol(CO_2)}{\pi r^2 h \rho} \quad \text{eq. 1}$$

where the numerator was calculated from integration under the CO<sub>2</sub> generation curve and sample mass was calculated from the laser sample dimensions ( $r$  = radius,  $h$  = sample depth) and the density ( $\rho$ ) of aragonite (2.93 g·cm<sup>-3</sup>)<sup>[12]</sup>, multiplied by a factor of 100 g·mol<sup>-1</sup> for conversion of weight to molecular quantity. A positive linear relationship between laser energy and CO<sub>2</sub> efficiency was observed (Figure 4). All subsequent laser samples were run at full laser power, imparting 25-33 J·cm<sup>-2</sup> to the aragonite surface. At this laser setting, approximately 30% of the material removed was converted to CO<sub>2</sub> by decomposition; the balance was presumably removed by ablation of CaCO<sub>3</sub> particles and possibly CO gas as in previous work.

Stable carbon isotope measurements were made using both the combination of masses 44-46 (ir-MS) and the direct comparison of masses 12-13 (AMS). Ratios between the former masses were used to calculate δ<sup>13</sup>C ratios using equations correcting for <sup>17</sup>O in a triple collector mass spectrometer <sup>[13]</sup>. Such a correction was not necessary for AMS determinations because carbon isotope ratios were measured directly from elemental ion beams rather than molecular ion beams. Stable isotope ratios measured by AMS were calculated using proportionality of current ratios to published ratios:

$$\delta^{13}C_{AMS,pro} = \left( \frac{R_{AMS}^{13}}{R_{PDB}^{13}} - 1 \right) \times 1000 \quad \text{eq. 2a}$$

$$R_{AMS}^{13} = \frac{\left( R_{OXI}^{13} \times r_{AMS}^{13} \right)}{r_{OXI}^{13}} \quad \text{eq. 2b}$$

where  $R$  represents an absolute isotope ratio from calculated or published values and  $r$  represents a measured isotope ratio. The AMS standard, OX I, was used as a laboratory standard and its absolute ratio was calculated from its value relative to VPDB (-19‰). In an AMS system, ratios of the ion currents do not represent absolute isotope ratios because a chopper wheel is used to render the  $^{12}\text{C}$  and  $^{13}\text{C}$  ion beam roughly equivalent in intensity to the  $^{14}\text{C}$  ion beam. These values, as well as those measured by ir-MS, are shown in Table 1. All sample  $\delta^{13}\text{C}$  ratios were significantly less than conventional phosphoric acid/ir-MS determinations which range between +4 and +5 ‰<sup>[14]</sup>, depending on whether the aragonite was formed before or after the commencement of the atmospheric  $\delta^{13}\text{C}$  Suess effect. Oxygen isotope ratios were measured externally by ir-MS and ranged between -39 and -71 ‰ VPDB. This large  $\delta^{18}\text{O}$  fractionation suggests significant formation of CO during laser decomposition. However, combustion of the gases at 800°C over a copper catalyst wire did not yield increased CO<sub>2</sub> efficiency. Gas composition was not tested using a mass spectrometer or gas chromatograph.

Radiocarbon ratios were corrected<sup>[15]</sup> for isotope fractionation using both stable isotope measurements. Age models based on  $^{230}\text{Th}$  in-growth in sclerosponge aragonite<sup>[16]</sup> were used to calculate age-corrected  $\Delta^{14}\text{C}$ <sup>[15]</sup>. These values are compared to values measured by conventional carbonate acid digestion methodology corrected to the same age models. Because the age-corrected  $\Delta^{14}\text{C}$  values are not constant through the basal aragonite skeleton, the overall comparison is made relative to the perturbation caused by global thermonuclear production of  $^{14}\text{C}$  in the mid 20<sup>th</sup> century. Figure 5 demonstrates that laser micro-sampled CO<sub>2</sub> produces a similar radiocarbon bomb curve to hydrolyzed CO<sub>2</sub>.

### *Discussion*

The efficiency of a laser micro-sampling device in producing CO<sub>2</sub> is significant. The laser used in this experiment is optimized for ablation, thus it was expected that CO<sub>2</sub> generating efficiency would be relatively low. An efficiency of 30% represents a maximum using this system (Figure 4), thus all subsequent sampling employed 100% laser power in order to replicate this

efficiency. It is likely that the shape of the laser pattern (spot, line, line of spots, raster of lines, etc.) could significantly change efficiency depending on spot size, depth of sample, rate of motion for scanning patterns, and repeated lasing of single locations on the surface.

Despite the efficiency determined herein, the ablation laser employed for these experiments is not an optimal sampling technique for radiocarbon work. Because it is designed for fine-scale sampling during ablation work, it is not designed to remove large quantities of material per unit time. Thus, the efficiency value of 30% represents a proportion of a very small amount of material removed per unit time. The rates of CO<sub>2</sub> generation in the fractionation experiments were in the vicinity of 1 μmol of CaCO<sub>3</sub> per hour. This resulted in exceedingly long sampling times for targeted amounts of approximately 5 μmol carbon (Table 1). In some cases, this target sample size was not reached and resulting measurements incurred an increased amount of analytical uncertainty (Table 1). A laser system that removes a larger amount of material per unit time could alleviate this problem without surpassing the “spot size” of a standard micro-milling bur. Further, it is likely that other lasers (most likely CO<sub>2</sub> lasers) would enable a greater efficiency in producing CO<sub>2</sub> from the material removed<sup>[3]</sup>.

During the longer-duration fractionation tests, the two deepest samples in the sclerosponge aragonite (Figure 1) display lower  $\Delta^{14}\text{C}$  values (Figure 5). It is unlikely that these values are representative of post-bomb return to pre-bomb levels of  $\Delta^{14}\text{C}$  – residence times of carbon in the ocean are too long. Figure 1 shows that these laser patterns are the deepest of those sampled; they both decomposed all of the aragonite and contacted the epoxy beneath. In the laser efficiency tests, CO<sub>2</sub> was not measurable when the aragonite was exhausted and the epoxy was being lased. However, the time of laser sampling during the efficiency tests was much smaller than the time of the fractionation tests due to the amount of material necessary for isotope measurement. The two youngest samples (Figure 5, top of Figure 1) would have shined on epoxy for a matter of hours during which each sample was being integrated. Efficiency tests only lasted tens of minutes at the longest. Assuming the epoxy is made from petroleum products and devoid of radiocarbon, it would not take a large amount to cause the decreased  $\Delta^{14}\text{C}$  values illustrated in Figure 5. Assuming that it decomposes slowly or minimally to CO<sub>2</sub>, the short-duration efficiency tests would have only generated a negligible amount of epoxy-resin sourced CO<sub>2</sub>.

Fractionation of carbon isotopes during laser sampling does not effect radiocarbon determination. Although AMS radiocarbon data are routinely corrected for isotope fractionation<sup>[15]</sup>, allowing comparison of contemporaneously formed materials as isotopically disparate as tree cellulose and marine carbonate, this is the first demonstration that radiocarbon values



from laser-generated CO<sub>2</sub> compare well to conventional methods of AMS carbonate measurement. Fractionation has been shown to be a hindrance to stable isotope measurements due to variability of fractionation depending on laser parameters and hole geometry<sup>[3, 8]</sup>. Furthermore, fractionation during thermal decomposition with laser radiation has been shown to vary with different degrees of decomposition of the parent mineral<sup>[11]</sup>, suggesting similar effects during laser decomposition. In the fractionation tests described herein, the laser was programmed to scan the mineral surface by moving the sclerosponge section under the laser at rates of 5 μm·s<sup>-1</sup>. This technique differed significantly in terms of reduced CO<sub>2</sub> efficiency compared to simply burning cylindrical holes in a stationary target (efficiencies were comparable with and without attempted catalyzed conversion of CO to CO<sub>2</sub>). Thus it is likely that fractionation of laser micro-sampled CO<sub>2</sub> observed in this experiment is caused at least in part to different laser patterns and scan speeds. Still, stable isotope values systematically became lighter towards younger samples (Table 1) indicating that all measurement techniques captured the δ<sup>13</sup>C Suess effect. Figure 5 illustrates that the resulting Δ<sup>14</sup>C values are comparable to phosphoric acid reaction values, no matter the δ<sup>13</sup>C determination method.

Fractionation of CO<sub>2</sub> produced by the laser did not vary with respect to stable isotope measurement technique. Both external δ<sup>13</sup>C measurements and AMS measurements of stable isotope ratios displayed variability (Figure 5), however there was no systematic bias in either of the measurement techniques or calculations. Ultimately, use of laser decomposition in conjunction with a gas-accepting AMS ionization source will mandate use of AMS δ<sup>13</sup>C measurements. In AMS systems, mass ratio measurements made between initial negative beams of <sup>12</sup>C and <sup>13</sup>C reflect stable isotope composition as well as mass interference of hydrides (mass 13 can be <sup>13</sup>C or <sup>12</sup>CH). All AMS systems modulate the amount of <sup>12</sup>C and <sup>13</sup>C beams permitted to enter the accelerator's Ar stripping canal where negative carbon ion beams are accelerated through a diffuse Ar cloud to strip away electrons and mass-interfering protons. As a result, positive ion beam current ratios measured after the stripping canal reflect isotope ratios, apportioned by the modulation of the ion beams because of ion current limitations that generally preclude the full <sup>12</sup>C beam from passing through the accelerator. In the NOSAMS system, AMS δ<sup>13</sup>C values are routinely only used as a first-order check on performance. The instrument is not tuned for stable isotope measuring performance equivalent to the ir-MS; thus uncertainties associated with AMS δ<sup>13</sup>C measurements (measured as the standard deviation of repeated ionization sequences of a single graphite target) were greater than ir-MS measurements by approximately two orders of magnitude. The overall effect of stable isotope uncertainty on Δ<sup>14</sup>C uncertainty is small; thus the large increase in

uncertainty associated with AMS stable isotope determination did not result in a proportionally large increase in  $\Delta^{14}\text{C}$  uncertainty (Figure 5). Nonetheless, in all applications measuring  $\text{CO}_2$  directly in an AMS system, more precise analysis of stable isotope ratios will be warranted.

It is not evident that heating of the evolved laser decomposition products in the presence of  $\text{O}_2$  yielded greater quantities of  $\text{CO}_2$ . Isotope fractionation is due to incomplete decomposition of  $\text{CaCO}_3$ ;  $\text{CO}$  and  $\text{O}_2$  are possible products away from the center of the sample pit formed by the laser, as is solid  $\text{C}^{[11]}$ . In all of these cases, fractionation can be expected to depend on the relative efficiencies of the system in producing each of these possible products. In the case that significant  $\text{CO}$  was produced, use of  $\text{O}_2$  to oxidize it would therefore simultaneously maximize the yield of  $\text{CO}_2$  and the efficiency of the system, and minimize carbon isotope fractionation between aragonite and  $\text{CO}_2$ . Because the former was not apparent as increased efficiency, it is concluded that the latter benefit was not achieved either. Thus,  $\text{O}_2$  and heat had no overall effects, positive or negative, on this experiment.

Efficiency results were replicated with Iceland spar (calcite) and fish otoliths (aragonite). These results illustrate the potential for using this technique on other substrates for radiocarbon analysis. In addition to laser decomposition, laser combustion AMS measurements could be attainable by allowing a limiting amount of  $\text{O}_2$  to enter the laser chamber during heating of cellulose such as tropical hardwood. This was not attempted as part of this project.

### *Conclusions*

Laser decomposition has been successfully employed to generating radiocarbon measurements from marine aragonite. Laser micro-sampling systems generally used for ablation of particles into ICP-MS provide significant  $\text{CO}_2$ -generating efficiency however they only remove very small amounts of material per unit time. Fractionation is not an issue of concern for laser decomposition AMS and AMS-measured  $\delta^{13}\text{C}$  is adequate for carbon isotope fractionation correction to  $\Delta^{14}\text{C}$  calculation. This method will undoubtedly open new lines of investigation into carbonates and, potentially, organic solids. To maximize the potential of the technique, future work is encouraged to investigate the use of either Nd-YAG lasers with bigger spot sizes or  $\text{CO}_2$  lasers with more  $\text{CO}_2$  generating efficiency. Our efforts revolving around the use of a Nd-YAG laser were more based on convenience than optimization of success. Our success in analyzing laser-generated  $\text{CO}_2$  defines a high potential for future development of this technique and coupling with gas-accepting AMS.

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## Figure and Table Captions

**Figure 1.** Laser transects in sclerosponge aragonite. **a:** Boreholes were lased through the sample thick section to calculate efficiency of laser in producing CO<sub>2</sub>. **b:** Thick section of a sclerosponge showing the difference between samples lased for ICP-MS samples lased for  $\Delta^{14}\text{C}$  ( photo: R. Parsley). Samples lased for  $\Delta^{14}\text{C}$  were precise but more intrusive than ICP-MS samples. The topmost laser samples in **b** were bored through the skeletal material to underlying epoxy – all other samples were not.

**Figure 2.** Experimental setup. A. Efficiency tests involved sweeping ablation and decomposition products through a 0.1 $\mu\text{m}$  in-line filter and a non-dispersive infrared CO<sub>2</sub> detector with He carrier gas for quantification of CO<sub>2</sub>. B. Fractionation tests involved the use of an in-line tube furnace between the filter and CO<sub>2</sub> analyzer to convert any CO to CO<sub>2</sub> at 800°C with a low flow of O<sub>2</sub> gas. After passing through the CO<sub>2</sub> detector, CO<sub>2</sub> was trapped and switched to a vacuum system for purification and manometric quantification before being sealed into Pyrex tubes under vacuum for isotope determination.

**Figure 3.** Efficiency test in sclerosponge aragonite. Efficiency of CO<sub>2</sub> generation by the laser was calculated as the amount of carbon dioxide integrated under the CO<sub>2</sub> detector curve, divided by the amount of calcium carbonate removed by the laser. Vertical lines indicate the limits of integration, but not necessarily the times of laser operation due to the low flow of gas through the relatively large laser compartment. The highest efficiency corresponded to the highest laser power (**Figure 4**).

**Figure 4.** Laser CO<sub>2</sub> efficiency versus laser energy. The linear fit through the data is forced through the origin because at the lowest tested settings for the laser (10 and 30% output), zero gas was produced. No forcing of the regression implies a blank (presence of gas without laser) which is not supported by the data.

**Figure 5.** Sclerosponge  $\delta^{14}\text{C}$  data from acid digestion and laser decomposition. Open circles show a time series of  $\Delta^{14}\text{C}$  measured by conventional phosphoric acid techniques. Closed circles illustrate the thermonuclear bomb curve measured by standard beta counting techniques in a sclerosponge and tuned to the atmospheric curve. Colored triangles indicate different  $\delta^{13}\text{C}$  correction techniques for laser  $^{14}\text{C}$  data. The two youngest laser points come from the deepest samples (**Figure 1**); all skeletal material was removed and the laser was in contact with epoxy and/or glass. Although this was not an issue during relatively short-lived efficiency tests, longer duration fractionation tests suggest that older carbon was mixed into the aragonite-generated CO<sub>2</sub>.

**Table 1.** Results from laser decomposition AMS and stable isotope measurements. Ages are calculated from  $^{230}\text{Th}$  activities of the sclerosponges as described elsewhere<sup>[16]</sup>. Sample sizes of  $\text{CO}_2$  were measured both manometrically and photometrically; manometric measurements are reported herein.

<b>Sample</b>	<b><math>\text{CO}_2</math></b>	<b>Distance from Surface</b>	<b><math>^{230}\text{Th}</math> Age</b>	<b><math>\delta^{13}\text{C}_{\text{ext}}</math></b>	<b><math>\delta^{13}\text{C}_{\text{AMS}}</math></b>	<b>Ocean Depth</b>	<b><math>f_M</math></b>	<b><math>\sigma_{fM}</math></b>
	<i><math>\mu\text{mol}</math></i>	<i>(<math>\mu\text{m}</math>)</i>	<i>y A.D.</i>	<i>‰ VPDB</i>	<i>‰ VPDB</i>	<i>m</i>		<i><math>1\sigma</math></i>
L-37	2.23	26500	1897	0	9	67	0.9691	0.012
L-38	8.98	250	1993	-5.4	-9.3	136	0.934	0.01
L-39	7.35	750	1990	-4	-7.2	136	1.0466	0.009
L-40	4	4150	1967	-4	-11.1	136	1.0559	0.0094
L-41	5.9	3500	1971	-2.1	-0.9	136	1.0846	0.0076
L-42	4	2750	1976	-3.3	1.5	136	1.1079	0.0118
L-43	6.6	7100	1947	-2.1	-5.5	136	0.9407	0.0078