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Beyond archaeology: ^{14}C -AMS and the Global Carbon Cycle

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Abstract. The Keck Carbon Cycle Accelerator Mass Spectrometer (KCCAMS) facility specializes in using radiocarbon (^{14}C) as a tracer for the global carbon cycle (GCC). KCCAMS distinguishes between natural and anthropogenic carbon found in natural waters, soils, sediments, the atmosphere, and biota. Presented here is an overview of our compact accelerator mass spectrometer (AMS) system. A brief description of technical modifications that allow us to obtain high beam current output from the ion-source ($\sim 225 \mu\text{A}$ of ^{12}C) and achieve high precision (0.2-0.3%), with minimum downtime for maintenance is also given. General requirements of ^{14}C -AMS sample preparation are summarized including recent advancements allowing the measurement of samples < 0.100 mg of carbon. In this review paper, the importance of the global carbon cycle and how the ^{14}C -AMS (as tracer) has assisted into understanding carbon exchange and cycling between the Earth's reservoirs – terrestrial, atmospheric, and marine – are succinctly illustrated and discussed.

Keywords: ^{14}C dating, accelerator mass spectrometry, global carbon cycle

PACS: 29.20.Ba, 29.25.Ni, 29.30.Ep, 88.05.Np

INTRODUCTION

In nature we can find three carbon isotopes, ^{12}C , ^{13}C and ^{14}C . Almost 99% of atmospheric CO_2 is constituted by ^{12}C , when smaller fractions such as 1.1% and 0.0000000010% are constituted of ^{13}C and the radioactive ^{14}C , respectively. Consequently, just one ^{14}C atom exists in nature for every 10^{11} ^{12}C atoms. The presence of ^{14}C in the atmosphere is due to the ongoing production by the interaction between cosmic rays and N atoms in the upper atmosphere. The ^{14}C atoms are oxidized to ^{14}CO and later to $^{14}\text{CO}_2$. The mean residence time of CO_2 in the atmosphere is about 5 years, allowing the newly produced $^{14}\text{CO}_2$ be mixed almost evenly in all parts of this reservoir. The ^{14}C particles are fixed in the living tissues of plants by photosynthesis and into other living organisms through the food web. The ^{14}C dating method relies on the fact that once this radioisotope is no longer replenished, its amount will decrease with time according to its half-life ($5,730 \pm 40$ years), as ^{14}C decays back to ^{14}N . Libby and coworkers [1] demonstrated that upon the measurement of the remaining ^{14}C from a “lifeless” or inactive organism, the time elapsed since its death could be then inferred.

The use of radiocarbon (^{14}C) dating has revolutionized archaeology, since it allowed researchers to assign an age to artifacts by measuring organic remains directly (e.g. the artifact themselves or material association with those). Before the ^{14}C method, events could only be determined as belong to some macro-scale framework

covering centuries, or putative ages from “guesswork” [2]. However, as any other approach, the Libby’s ^{14}C method is based on series of assumptions. Therefore, the interpretation of ^{14}C data needs to be made with awareness of the following issues [3]: (a) the natural variations in the atmospheric ^{14}C content cause the radiocarbon clock to run differently in comparison with the “real calendar time”, consequently ^{14}C ages must be calibrated; (b) each of the 3 types of photosynthesis (C3, C4 and CAMS) utilized by plants fractionate C isotopes differently, due to differences in stomata management. Consequently, the ^{14}C age must be corrected for the mass-dependent fractionation (obtained through the measurement of $\delta^{13}\text{C}$); (c) living organisms in the marine reservoir shows an offset in ^{14}C age in comparison with contemporaneous organisms from the terrestrial environment, and therefore they require correction; and (d) anthropogenic effects (dilution of atmospheric ^{14}C by combustion of fossil fuels and increasing atmospheric ^{14}C concentration from nuclear bomb tests) also had altered the ^{14}C in the global reservoirs. The fact that most of Libby’s basic assumptions (described above) did not necessarily hold, allowed a series of natural geochemical C processes studies to be launched. Libby’s basic assumptions are the driver of ^{14}C as a tracer in the GCC.

In 1977, the ^{14}C method faced a major breakthrough. The AMS technique allowed the amount of ^{14}C in the sample to be measured directly [4, 5], reducing its size for a measurement by a factor of 1,000 compared to the sizes required for decay counting methods. In addition, samples could be measured in a few minutes instead of days.

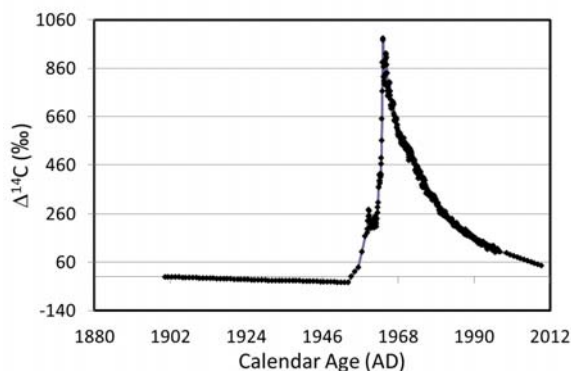


FIGURE 1. $\Delta^{14}\text{C}$ values for the compiled Northern Hemisphere “bomb curve” [6-9].

With a good understanding of Libby’s early assumptions and its “palliative” corrections, it is feasible today to assign accurate ages to artifacts, bones and strata (e.g. ± 20 years on samples younger than 10ka years BP; “Before Present” (or before 1950), the arbitrary calendar age origin of the ^{14}C scale). The ^{14}C method remains the most reliable dating technique for the late Pleistocene and Holocene periods. Besides the obvious beneficiaries of the ^{14}C -AMS “duet” (archeologists), other science fields readily realize the small size gain of the AMS technique. Moreover, thanks to the amount of ^{14}C produced by atmospheric weapons testing (Fig.1), the enriched ^{14}C could be traced as it dissolves in surface seawaters and advances into the oceans, or when fixed and respired by terrestrial organisms. This capability makes ^{14}C -AMS one of the most powerful tools to quantify exchange rates of C between reservoirs (ocean, land and atmosphere), potentially yielding clues to future climate change.

In this review, a brief description of the capabilities of our AMS facility is provided alongside general aspects of the ^{14}C -AMS sample preparation. The importance of the GCC and how ^{14}C -AMS has increased understanding of C exchange and cycling between the Earth's C reservoirs are illustrated and discussed.

THE KCCAMS/UCI FACILITY

In 2000, researchers of the Earth System Science (ESS) department at University of California Irvine (UCI) recognized the need of a better understanding of the natural C cycling and its interactions with the climate system to then, predict global climate changes. The Keck Carbon Cycle AMS facility (KCCAMS) based on a compact AMS system (Fig. 2) and sample preparation laboratories were then established in 2002, with the goal of studying the Earth's C cycle through the use of ^{14}C as a tracer.

Our AMS system is equipped with large Cryopumps (Cryotorr 8) instead of turbo pumps, and the NEC 40-sample MC-SNICS cesium sputter ion-source that produces negative ions from solid graphite targets. This unit possesses a fast beam switcher in the injection system allowing us to sequentially inject ^{12}C , ^{13}C and ^{14}C into the electrostatic accelerator, cycling through these isotopes 10X per second. This feature provides fractionation correction (e.g. the $\delta^{13}\text{C}$ online values) to ^{14}C values for any isotopic shifts induced by the spectrometer as well as the natural and sample preparation combined. This system has undergone several modifications. Because ion source output determines spectrometer throughput, initial modifications from 2002 to 2006 were focused on the ion source [10-13]. Later, we also modified the beam transport system and small sections within the accelerator [14-15]. Those combined changes and improvements (briefly described below) allow us to measure nearly 1,000 samples per month with accuracy and precision in the range of 0.2-0.3%.

I) A sliding track system was built into the existing power supply rack to allow easy servicing in-situ. A stainless-steel/copper wheel with large aluminum (Al) front loading holders, which is very easy to clean since it does not build up Al oxide layers, was designed to replace the one sold by NEC. The entire process of cleaning the source, exchange ionizer, and extractor assemblages, baking out the system, achieving proper vacuum, then outgassing, requires < 6 hours (every few weeks).

II) The internal extractor and lens electrodes were rebuilt to increase pumping efficiency. All aluminum parts were replaced with stainless steel to improve cleaning. We also replaced the NEC pre-acceleration tube downstream of the extraction assembly with a larger fully shielded Ceramaseal insulator. The pumping conductance increased by a factor of 3, leading to reduction in the evacuation time required after sample wheel changes (< 1 hour between wheel change and starting of a new tuning);

III) A redesigned stainless steel ion-source body with extra inner cooling accommodates a modified Cs housing combined with spherical ionizer, oven and delivery tube. Those features allow a better control and focusing of the Cs. Beam currents of $\sim 225 \mu\text{A}$ of $^{12}\text{C}^-$ at 8.5 kV are routinely achieved;

IV) The original injector magnet was redesigned to increase the gap, and therefore accommodate a new magnet box of 68 mm. The purpose of this change was to allow larger (higher divergence) ion beams to be transmitted;

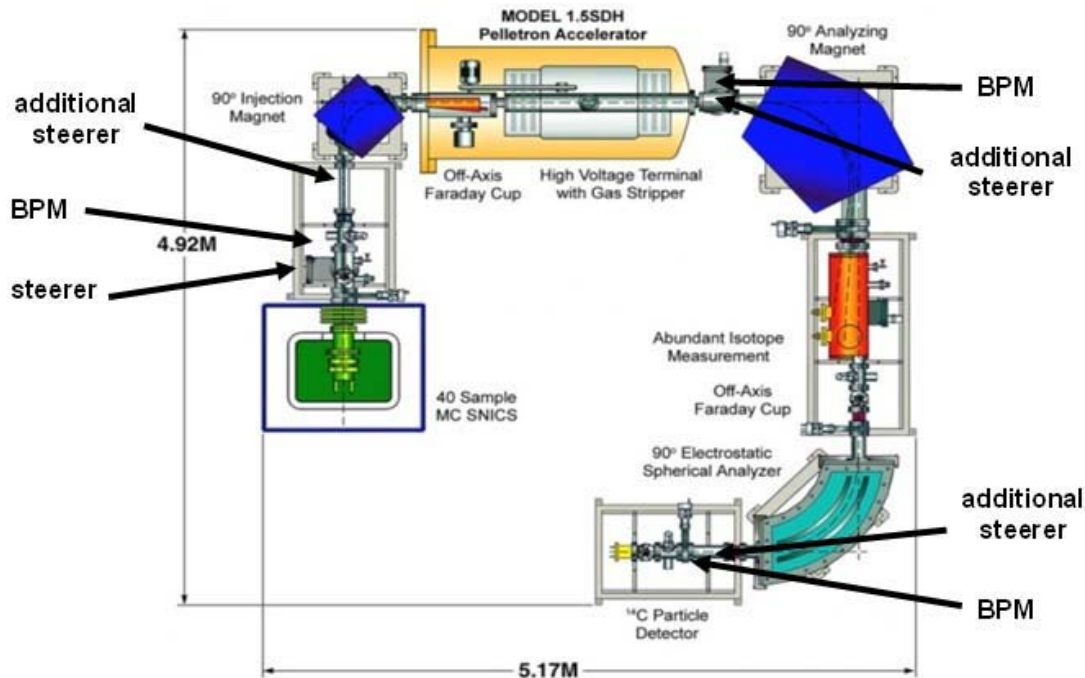


FIGURE 2. The layout of our NEC-0.5MV-1.5SDH-1 AMS system and its specific features.

V) In the accelerator, we managed to increase charging currents (30%) by replacing the rims of the drive and high voltage terminal pulley with new conductive plastic versions. Consequently, a reduction in “tank” dust generated by arcing and erosion of the pulleys was achieved (tank opening and cleaning - every ~9 months);

VI) The NEC current integrators that measure the stable isotope currents were recalibrated, improving linearity when measuring samples as small as ~0.010mgC. Source efficiencies of 10-15% for 0.005-0.010mgC sample sizes, indicating that 1% precision measurements are possible with near modern samples.

The ¹⁴C-AMS sample preparation (general aspects)

The KCCAMS labs can process samples from several organic and inorganic pools (e.g. from solid carbonaceous materials to particulate and dissolved C fractions from air or water) [16]. We can also isolate and measure ¹⁴C of organic biomarkers (such as sugars, lipids, etc), plus single compounds from sample matrices, which normally produces sub-milligram samples of << 0.100mgC. Our ability to measure ultra-small samples is a consequence of: a) our relatively “high” C⁻ beam currents of 1 μA per μg of C for samples in the 0.002 to 0.010 mgC range; b) understanding and correcting machine-induced isotopic fractionation as well as exogenous C introduced during sample processing; and c) producing close to 100% reaction yield ¹⁴C-AMS graphite samples [16]. Once carbonaceous “raw” materials are decontaminated or isolated, they are converted into CO₂, which is then reduced to graphite [17, 18], pressed into holders, loaded into the AMS for measurement.

Careful sampling and adequate pre-treatment (physical and chemical - to purify the sample) are essential steps of the ¹⁴C dating process. The pre-treatments applied vary according to the nature and status (stages of preservation) of the material to be dated

[19]. We maintain quality control through the long-term evaluation of methodologies by assessing accuracy and precision with known age standards from the NIST, IAEA, TIRI and FIRI series [16, 20]. In addition to standards, it is important to evaluate blanks (i.e. those whose ^{14}C content is known to be beyond AMS detection limits or $\gg 10$ half-lives) alongside the unknown samples. Frequent evaluation of those “blind” samples is essential for capturing the variability arising from different sample procedures and to quantify the C introduced during sample processing [20].

THE GLOBAL CARBON CYCLE

Carbon is naturally cycled among its main three reservoirs, the atmosphere, the oceans and biosphere. The dynamic processes by which C is exchanged from one reservoir to another take place on different time scales. Time scales found in photosynthesis, plant and animal respiration, and the movement of carbon dioxide (CO_2) across the air-sea interface can extend from seconds to decades (the short-term C cycle), while transformation of C into limestone and fossil fuel build up take thousands to millions of years (the long-term C cycle). The C cycle and its balance are vitally important to life on Earth and its climate. Carbon-containing compounds in the atmosphere (such as CO_2 , methane (CH_4), carbon monoxide (CO), and chlorofluorocarbons (CFCs)) work as a temperature-regulation system [21].

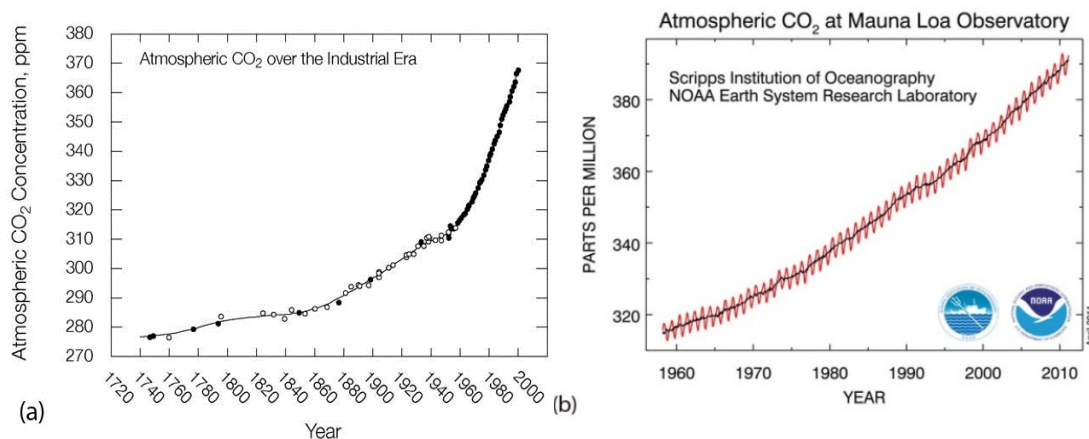


FIGURE 3. (a) Concentration of atmospheric CO_2 , in ppm, from 1740 to 2000 [23, 24]. A quick rising of CO_2 levels in the atmosphere at remote locations on Earth (e.g., the South Pole and the summit of the Mauna Loa volcano in Hawaii) is noticeable. (b) The full Mauna Loa CO_2 record today (<http://www.esrl.noaa.gov/gmd/ccgg/trends/>).

Recently it has been recognized that anthropogenic activities, starting mostly during the industrial revolution, are altering the Earth's climate [25]. Direct impacts on the global climate system are related to pollution, land manipulation/alteration, and increasing concentrations of airborne particles and greenhouse gases (mostly CO_2). Figure 3 illustrates the amount of CO_2 in the atmosphere today with respect to its natural values [26]. This increase is mostly associated with burning of fossil fuels (e.g. an unnatural and fast release of C that was stored by the long-term C cycle process).

Temperature increases due to increased CO₂ concentrations are expected to be 1.4–5.8°C by the end of this century [25], leading to dramatic impacts to the climate system and societies (e.g. sea level rising between 10–90cm, leading to the loss of many coastal habitats; increased frequency or severity of climate hazards, such as cyclones, tornados, hurricanes, floods and drought, cold and heat waves; expanding the range of disease carriers; among many others).

Radiocarbon and the oceans

A comprehensive investigation of the world oceans and their close interaction with the atmosphere is illustrated in Fig. 4. The high resolution data shown in the cited studies is in part due to the capability to analyze small samples. Over 250 liters of seawater sample were required for a ¹⁴C measurement prior to the-AMS era; just 0.5 l was needed after. Ongoing dissolved inorganic carbon (DIC) ¹⁴C and δ¹³C measurements of seawater (WOCE) from the Southern, Indian, Pacific and Atlantic oceans has reached a total of 20,000 samples as of 2008 [27]. These ¹⁴C results show how the ¹⁴C “bomb peak” is diffusing in the water column, and are vital if we are to monitor any changes in oceans circulation.

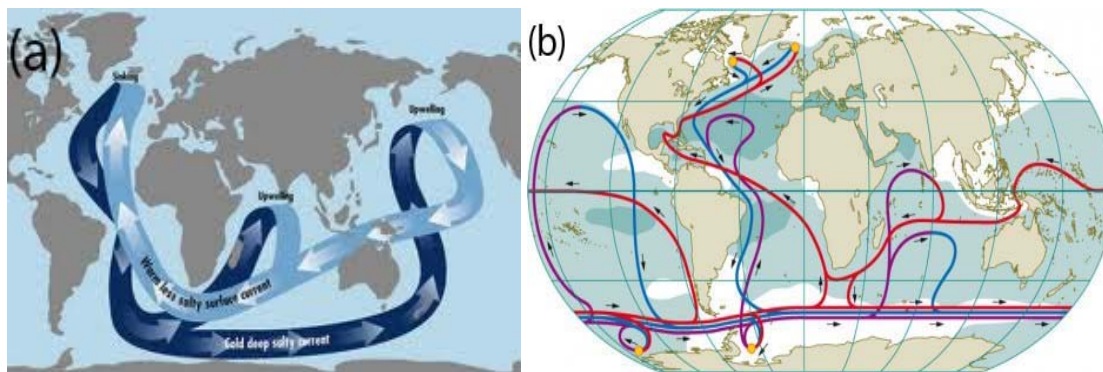


FIGURE 4. (a) The great ocean conveyor belt; a simplified diagram of the main ocean current that transports heat around the globe. (b) The complex worldwide ocean currents of the thermohaline circulation system. Some researchers believe the stabilization of this great current was responsible to keep the planet from continuing on ice/hot age shifts at about 10ka years ago. A disruption of this current due to global warming might bring dramatic climatic shifts back [28, 29].

Radiocarbon and the atmosphere

The atmosphere is the smallest pool of actively cycling C (less than 1%, when compared with the oceans and the biosphere); however it is the main entrance of C into the system. Using bomb-derived excess ¹⁴C (Fig. 1), natural redistribution of C between reservoirs could be thoroughly studied. Radiocarbon has been used to study atmospheric mixing, air-sea gas exchange rates, oceanic uptake of anthropogenic CO₂, and C turnover rates in various ecosystems. Depleted values of ¹⁴C in the atmosphere (early 1900 to 1950) were first observed by Suess when measuring ¹⁴C in tree rings with a precision between 15–25‰ [6]. The effect, that is ongoing until today, was then masked by the nuclear test weapons during 1953 to 1963. After the ban, the

atmospheric ^{14}C concentrations decreased rapidly through uptake by other large C sinks (oceans, and biosphere), and by dilution with old C produced from the burning of fossil fuel. The “bomb peak” curve (Fig. 1) is an excellent example of the use of ^{14}C in the atmospheric reservoir. Though current gradients are much smaller today (as the excess ^{14}C is basically gone), variation in $^{14}\text{CO}_2$ will continuously reflect C exchanges within this and the other reservoirs. Thanks to the advantage of the ^{14}C -AMS “duet”, ^{14}C measurement precision today on $^{14}\text{CO}_2$ can be as good as $\pm 2\%$ [9].

Radiocarbon and the biosphere

Within this reservoir millions Gt of C is currently stored in sedimentary rocks (mostly limestone) and fossil fuel reservoirs, in addition to plants and soils. Plants and soils store and release C on time scales ranging from seconds to thousands of years, and although its storage capacity is far smaller (~ 2 Gt) than the full reservoir itself, it has been actively modified by humans. Due to biosphere diversity it has been difficult to calculate the magnitude of its role to the GCC.

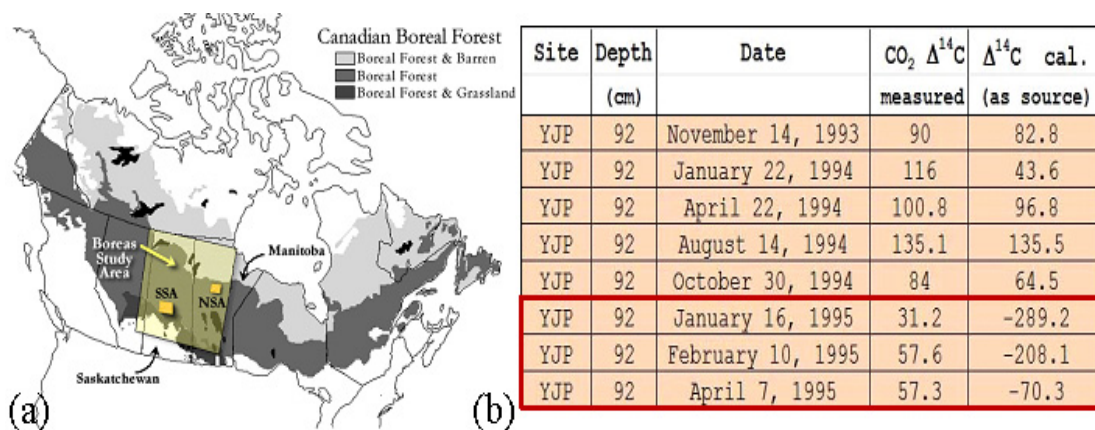


FIGURE 5. (a) Map of Canadian Boreal Forest highlighting the areas of study. (b) The $^{14}\text{CO}_2$ values measured at depth of 92 cm under young jack pine (YJP) [30]. During the cold season CO_2 $\Delta^{14}\text{C}$ values become depleted (highlighted) as upper layers “shut down” due to atmospheric lower temperatures near to soil surface. It seems that only the “warmer deep layers” are capable to maintain C decomposition. The combined ^{14}C value of the old C pools is $\sim 2,7\text{ka}$ yrs BP ($\Delta^{14}\text{C} = -289.2\%$, during January 1995).

To understand fluxes and sources of CO_2 during the snow-covered season, that contribute to the annual C budget, researchers measured ^{14}C -AMS from soil respiration at sites within the Canadian boreal forest (Fig.5a), under three ecotypes (old black spruce, old jack and young jack pine) [30]. The ^{14}C -AMS results (Fig. 5b). suggested that the CO_2 respired from different soil depths during the colder seasons was not simply the C fixed during the previous growing season, but instead originated from a mixture of fast cycling and slow cycling C (thousands of years old stored at depth). This findings show how the temporal pattern in CO_2 flux changes, reaching a minimum when atmospheric temperatures are at the lowest in mid-winter, allowing deep-old soil CO_2 be released. A more persistent inter-annual trend to warmer winters, due to global warming, could potentially enhance this old source of C to atmosphere (increasing even further its C budget).

CONCLUSION

Radiocarbon has found widespread use in understanding past climates and the GCC. In paleoclimatic studies, ^{14}C provides information on the age of C that has been stored in the deep oceans, as well as in C found in soils and sediments. This information can aid in reconstructing the past natural climatic variability. Bomb peak ^{14}C has been utilized in studies of atmospheric CO_2 inputs to ocean and terrestrial systems, and for understanding partitioning, and turnover of C within those systems.

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