Palaeoart and Materiality

The Scientific Study of Rock Art

edited by

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ARCHAEOPRESS ARCHAEOLOGY

Archaeopress Publishing Ltd
Gordon House
276 Banbury Road
Oxford OX2 7ED

www.archaeopress.com

Cover image: Part of the Huashan site in Guangxi Province, southern China, the largest rock painting site in the world. Photograph by R. G. Bednarik.

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A new low energy plasma system laboratory at the Center for New Mexico Archaeology (Santa Fe, New Mexico) for radiocarbon sampling has recently been established. Significant improvements to previous systems have been instituted, not only in the system itself, but also in experimental procedures. Multiple chambers for sampling have been added to increase efficiency. Dual internal secondary argon and oxygen storage chambers are added for quick refilling purposes. Masking procedures are also being tested to isolate specific carbon-bearing material from the rest of sample in the form of aluminium foil or alumina (aluminium oxide powder).

Nuevo sistema de plasma frío para la toma de muestras de ^{14}C en pictogramas

Recientemente se ha desarrollado un nuevo sistema de plasma de baja energía para la toma de muestras de radiocarbono en el laboratorio del Centro de Arqueología de Nuevo México (Santa Fe, Nuevo México). Se han efectuado mejoras significativas respecto de los sistemas anteriores, no sólo en el propio sistema sino también en los procedimientos experimentales. Se han añadido múltiples cámaras de muestreo para aumentar la eficiencia. A fin de facilitar la rápida recarga se añaden cámaras secundarias internas de almacenamiento dual de argón y oxígeno. También se están probando procedimientos de enmascaramiento específicamente para aislar el carbono del resto de la muestra en forma de papel de aluminio o alúmina (óxido de aluminio en polvo).

The development of radiocarbon dating in the mid-twentieth century revolutionised archaeological chronology (Libby 1955; Wood 2015). The combination of relatively simple theory and the ability to estimate relative isotope abundances resulted in the generation of reliable age estimates for samples of organic carbon from archaeological contexts. In the ensuing decades, the power of radiocarbon dating has increased dramatically. Archaeologists are now much more sophisticated in understanding underlying principles, leveraging that knowledge into a far more reliable selection of samples and interpretation of results. The calibration of atmospheric variation in cosmogenic radiocarbon levels has resulted in much improved calendric date range interpretations, and isotope measurement with accelerator mass spectrometry (AMS) has reduced the size of samples, allowing dating based on annual plant parts.

Accelerator mass spectrometry for carbon-14 dating was introduced essentially simultaneously from three different laboratories in 1977 (Bennet 1977; Muller 1977; Nelson et al. 1977), allowing the possibility of radiocarbon dating of rock paintings for the first time. However, it was another decade before the first successful attempt to radiocarbon date charcoal pigments from pictograms from Africa (Hedges et al. 1987; Van der Merwe et al. 1987). This African rock art date was followed quickly by other investigators from several laboratories and rock art sites (Loy et al. 1990; McDonald et al. 1990; Russ et al. 1990; Valladas et al. 1990). Considerable progress has been made since those first radiocarbon dates, as well as some of these earlier, and some later, measurements have not stood the test of time.

Plasma extraction

Introduced in 1990 (Russ et al. 1990), the plasma extraction technique has been utilised for the past two and a half decades to obtain a few hundred dates on rock paintings around the world (see reviews by Rowe 2005, 2009, 2012; Steelman and Rowe 2012). Over the next several years, four more generations of plasma systems were built at Texas A&M University (Russ et al. 1993; Chaffee et al. 1993a, 1993b; Ilger et al. 1994b), and additional rock art dates have continued to be produced (Hyman and Rowe 1992; Russ et al. 1992; Chaffee et al. 1994a, 1994b, 1994c; Ilger et al. 1994a, 1994b, 1995, 1996; David et al. 1995, 1997, 1998, 1999, 2001; Armitage et al. 1997, 1998, 2000a, 2000b, 2000c, 2001, 2005; Hyman and Rowe 1997; Hyman et al. 1999; Pace et al. 2000; Diaz-Granados et al. 2001, 2015; Steelman et

al. 2001, 2002a, 2002b, 2002c, 2004, 2005; Rowe 2003, 2005; Rowe and Steelman 2003, 2004; Rowe et al. 2001; Jensen et al. 2004; Scott et al. 2005; Brock et al. 2006; Hunter-Anderson et al. 2013; Boyd et al. 2014; Duncan et al. 2015).

A significant advantage of the plasma technique is that the inorganic rock substrate (often including carbonates) does not decompose during exposure to low energy oxygen plasmas. This eliminates the need to use extensive acid pretreatments because the plasma temperatures used (< 150°C) are below the decomposition temperatures of both carbonates and oxalate minerals, and only organic carbon is extracted from a sample for radiocarbon measurement (Russ et al. 1992; Chaffee et al. 1993a). Later research added the argument that plasma oxidation is preferable to conventional acid pretreatments because acid washes may not completely remove oxalate minerals, which are commonly associated with rock surfaces and which would contaminate conventional radiocarbon dates (Hedges et al. 1998; Armitage et al. 2001).

The plasma technique is particularly well suited to non-charcoal pigments. The organic matter being dated is presumably derived from binders or vehicles that were added to the mineral pigments when the paints were made and applied. The plasma technique is effective for sampling binders because of the extremely small samples needed for direct AMS dating of CO_2 (only 40–100 micrograms of carbon are needed). Sufficient carbon for dating has been extracted from red, yellow, brown, purple, and black non-charcoal paints. This potential continues to be explored by Professor Karen Steelman in her laboratory at the University of Central Arkansas and by Professor Ruth Ann Armitage at Eastern Michigan University.

Plasma oxidation has successfully dealt with many issues of rock art dating although some concerns still remain (Rowe 2007, 2009; Rowe and Steelman 2003b; Steelman and Rowe 2012). Since its inception, plasma-chemical carbon extraction has been used to date rock paintings from all around the world. At least one pictograph has been dated by the plasma oxidation technique in Arizona, California, Colorado, Idaho, Missouri, Montana, New Mexico, South Dakota, Texas and Wisconsin. The following countries also have pictograms dated by the plasma oxidation technique: Angola, Australia, Belize, Brazil, Dominican Republic, France, Guam, Guatemala, Mexico, Nicaragua and Spain.

Rock art research had been minimised in the years before dating was possible, reliable methods to date the ancient imagery have moved it toward mainstream archaeology, and we expect that trend to continue unabated and more reliability can be assigned to the dating techniques that are being used.

The New Mexico Plasma Laboratory

The newest low-energy oxygen plasma radiocarbon sampling laboratory has been built at the Center for New Mexico Archaeology (CNMA) in Santa Fe, New Mexico. The basic architecture of the apparatus is a high vacuum system that is capable of achieving and maintaining vacuums of at least 10^{-6} torr (Fig. 1). Glass sample chambers of various sizes (diameter 18–114 mm) are attached to the vacuum systems and to manifolds for the introduction of both high-purity oxygen and argon gases for cleaning and sampling steps. Plasmas are generated at gas pressures of 3 torr using an RF generator (13.56 MHz) where we have maintained power levels as low as 5 watts and chamber temperatures of 35°C or less. After gas samples are generated by plasma oxidation, water vapour is separated with a dry ice-acetone trap, and the CO_2 for radiocarbon dating is then condensed within a 4 mm outside diameter glass tube using a liquid nitrogen bath. The glass tube is flame-sealed, retaining the CO_2, and the ampoule is separated from the apparatus for shipment to the ETH Zurich AMS laboratory under the direction of Lukas Wacker. ETH Zurich is capable of the direct AMS dating of CO_2 samples of 40–100 micrograms, bypassing the need for graphite conversion (Fahrni et al. 2013; Ruff et al. 2007; Wacker et al. 2013.

The challenge of plasma radiocarbon sampling is minimising the risk of any contamination from modern carbon. After evacuating the empty sample chamber to a vacuum of ~10^{-6} torr, research purity oxygen is introduced at a low pressure (3 torr). Initial oxygen plasma cleansings of the chamber are then carried out to eliminate any extraneous contaminating carbon from the previous run or from handling of the chamber between runs. The sample to be processed is then placed into the chamber. Samples can be introduced as chunks of painted substrate, as paint flakes, or as powders. Substrates need to be analysed separately in addition to analysing painted substrates in order to rule out the presence of contaminating organic carbon within the substrate. After introduction of the sample into the sampling chamber, contamination from modern atmospheric CO_2 must be minimised, both as ambient gas in the system (removed with the high vacuum) and as CO_2 that may be adhering to the surfaces of the sample and the chamber. After evacuating the sample chamber, research purity argon is introduced at low pressure (3 torr). The sample is bathed in argon plasmas (usually 25–35 watts and at temperatures of ~100°C for rock art samples). Argon is close to CO_2 in molecular weight, and the plasma scours the sample and the surfaces of the apparatus, dislodging adhered CO_2. In addition to the adsorbed CO_2 the sample can also release water vapour, absorbed CO_2 and other gases, and unknown compounds that may be volatile under warm low vacuum conditions. Chamber pressure is monitored after each argon plasma run after the application of liquid nitrogen, characterising the amount of evolved
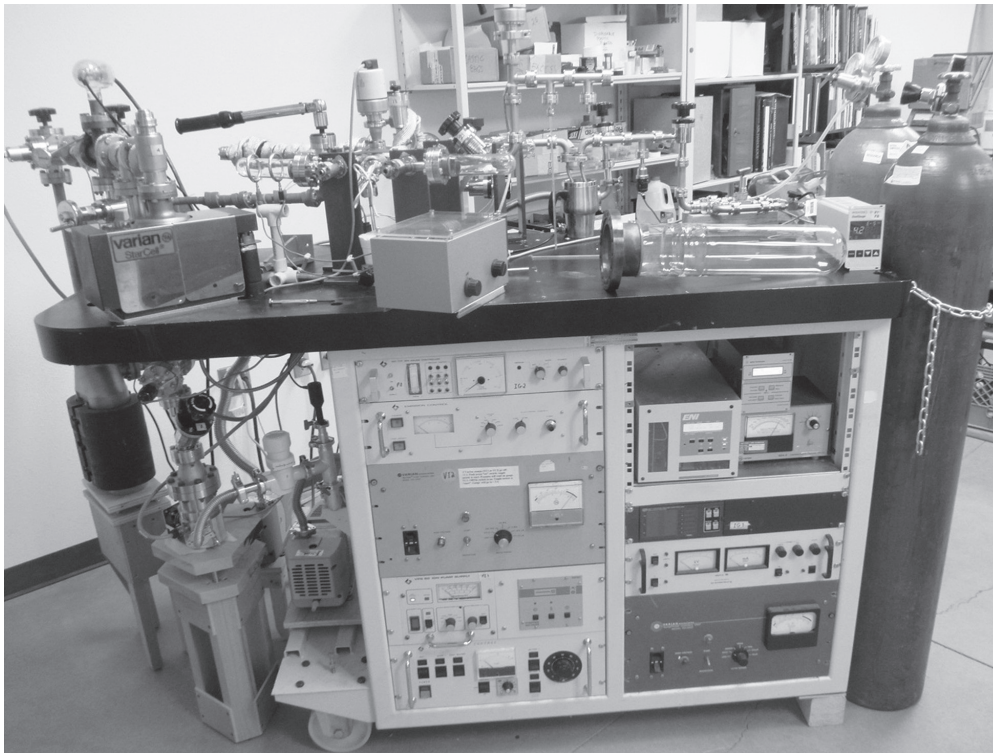
FIGURE 1. OVERVIEW OF THE PLASMA SAMPLING APPARATUS AT THE CENTER FOR NEW MEXICO ARCHAEOLOGY.

or liberated potential contaminants (principally carbon dioxide); the argon plasma cleaning step is repeated as often as necessary to eliminate significant remaining contamination. When less than 0.5 micrograms of carbon as carbon dioxide is captured, the sample is now ready to be processed using the plasma oxidation technique. Since the argon cleaning stage is not chemically reactive, little if any carbon is being removed from the material other than as absorbed or adsorbed CO_2. The exception may be rare samples whose composition includes hydrocarbon compounds that can be volatilised at the low operating temperature and pressure of the plasma.

Following the argon cleaning stage, low pressure (3 torr) research-purity oxygen is introduced. A low energy oxygen plasma is initiated in the chamber (usually 25–75 watts and <90°C for rock art samples), and the plasma is maintained for as long as is necessary to produce at least 40–100 micrograms of carbon in the form of CO_2. In addition to sample size, sample surface area affects the amount of carbon that is oxidised irrespective of the amount of time that the plasma is running. Water vapour and traces of other gases are produced in addition to CO_2. When sufficient CO_2 has been created, the plasma is turned off, and the accumulated gas is subjected first to a liquid nitrogen trap to capture whatever gases have been created in the chamber (primarily CO_2). After 10 minutes the liquid nitrogen bath is removed and a dry ice-acetone trap is initiated in order to separate water vapour and other temperature-specific contaminants while releasing

the accumulated CO_2 into the closed system. After determining that sufficient gas has been captured, the gas is subjected to another liquid nitrogen trap to concentrate the CO_2 within a 4-mm outside-diameter glass tube. Pressures are monitored to ensure that adequate carbon has been produced, and then the tube is sealed into an ampoule and separated from the apparatus. Multiple CO_2 oxidation samples can be collected as back-ups if needed and if enough binder/vehicle is present in the rock art sample.

New innovations added to the New Mexico plasma system

Masking

Composite materials pose challenges to radiocarbon dating, both within and outside the context of non-destructive approaches to sampling. A feature of plasma oxidation is the expectation that direct exposure to energised oxygen species is necessary for the release of organic carbon from the object being sampled. Exposure to non-energised oxygen molecules should not result in oxidation, and those carbon components should not be included in the radiocarbon sample. This expectation raises the possibility of masking objects to be sampled, allowing the sampling of only a pre-selected portion of an object by covering non-selected portions with a covering or coating that prevents contact with energised species.
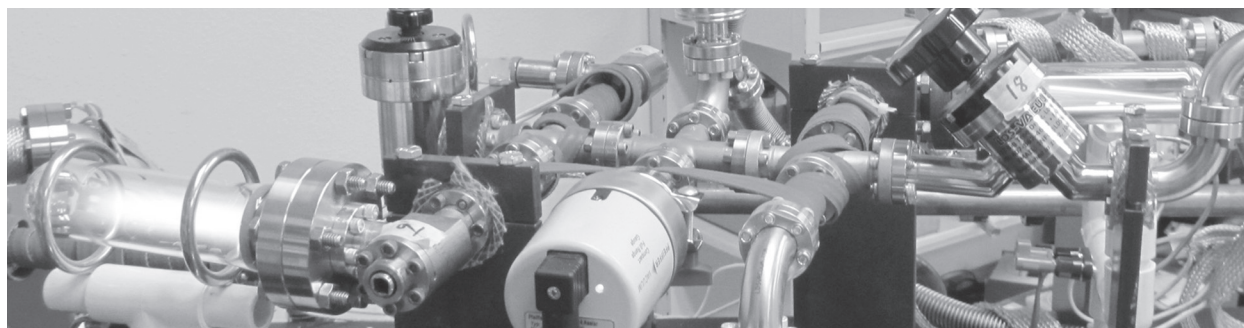
FIGURE 2. SIMULTANEOUS RUNNING OF TWO ARGON PLASMAS WITH RING RF ELECTRODES (LEFT) AND BAR ELECTRODES (BACK RIGHT).

Potential applications include the radiocarbon dating of different components of the same painting sample or masking off potential background contamination from a substrate. Two masking approaches are currently being investigated. The first simply uses high-purity aluminium foil that is shaped around the sample so that only the painted area of interest is exposed to the plasma. Oxygen species penetrating beneath the foil should lose energy and become non-reactive with carbon compounds that have been protected by the mask. The other approach will be to use a painted-on suspension of inert material (such as aluminium oxide powder). Similarly, oxygen species that diffuse through the porous powder coating are expected to be non-reactive by the time they reach the underlying surface. Both masks can be removed or reset to allow the collection of radiocarbon samples from different areas of complex artefacts.

AMS samples masked using aluminium foil have been successfully collected and dated, but more research needs to be done to demonstrate how effective the technique is in complex situations. If these masking approaches prove to be effective, masking will certainly dramatically increase the potential applications of plasma sampling for radiocarbon dating, perhaps even including rock art samples where substrates are currently too 'dirty' to date in terms of contributing organic carbon that is not contemporary with the pigment applications.

Simultaneous chamber plasmas

In an effort to increase efficiency and productivity, we have incorporated four plasma chambers into the sampling system. Our aim is to be able to run all four of the plasma chambers simultaneously. We have been able to successfully run two chambers simultaneously with a single one-radio-frequency generator, and an example of simultaneous plasmas is shown in Figure 2. We anticipate that incorporation of four new, smaller RF tuners will facilitate the operation of all four plasmas simultaneously, but there also appear to be some useful power-temperature relationships from the simultaneous operation of multiple chambers from a single RF tuner.

Internal oxygen and argon storage chambers

Another improvement to the New Mexico device has been the addition of internal storage of the pure argon and oxygen gases. Incorporation of storage chambers into the plasma system alleviates the necessity to go through the rather lengthy and laborious process of filling the plasma chambers from high pressure tanks for each run. This saves about 45 minutes on each plasma run, substantially increasing the efficiency of routine plasma operation.

Calibration of the New Mexico plasma apparatus

In May of 2015, a series of calibration samples was submitted to the AMS laboratory at ETH Zurich for radiocarbon dating using a gas ion source for direct insertion of carbon dioxide (Fahrni et al 2013; Ruff et al 2007; Wacker et al 2013). These included CO_2 from the TIRI/FIRI Belfast wood standard (including a sample collected as part of the plasma run with the distillation effect described above, ETH61251.1). Results are presented in Figure 3. The FIRI consensus date is 4508 BP for all measurement methods, while the consensus date for ages estimated by AMS measurement is 4519 BP (Scott 2003: Table 7.1). The mean of the four New Mexico dates is 4545 BP, in agreement with the FIRI inter-laboratory comparison results. The New Mexico results are also consistent with dates produced from other plasma-collected samples from other laboratories (see Fig. 3), including the tendency for mean dates to be slightly older than dates for samples collected and processed by other techniques.

Risks of contamination in plasma oxidation sampling are ever present due to potential failures of vacuum seals and the contamination of argon or oxygen gas contamination. Routine checks for both are built into the chamber and sample cleaning runs, where sampling is not initiated until potentially contaminating CO_2 from any source is less than 0.5 micrograms. Routine re-sampling of standards, including both the TIRI Belfast pine and a dead carbon source, are built into the laboratory schedule to confirm the reliability of the CNMA sampling technique and the accuracy of the associated radiocarbon dates.
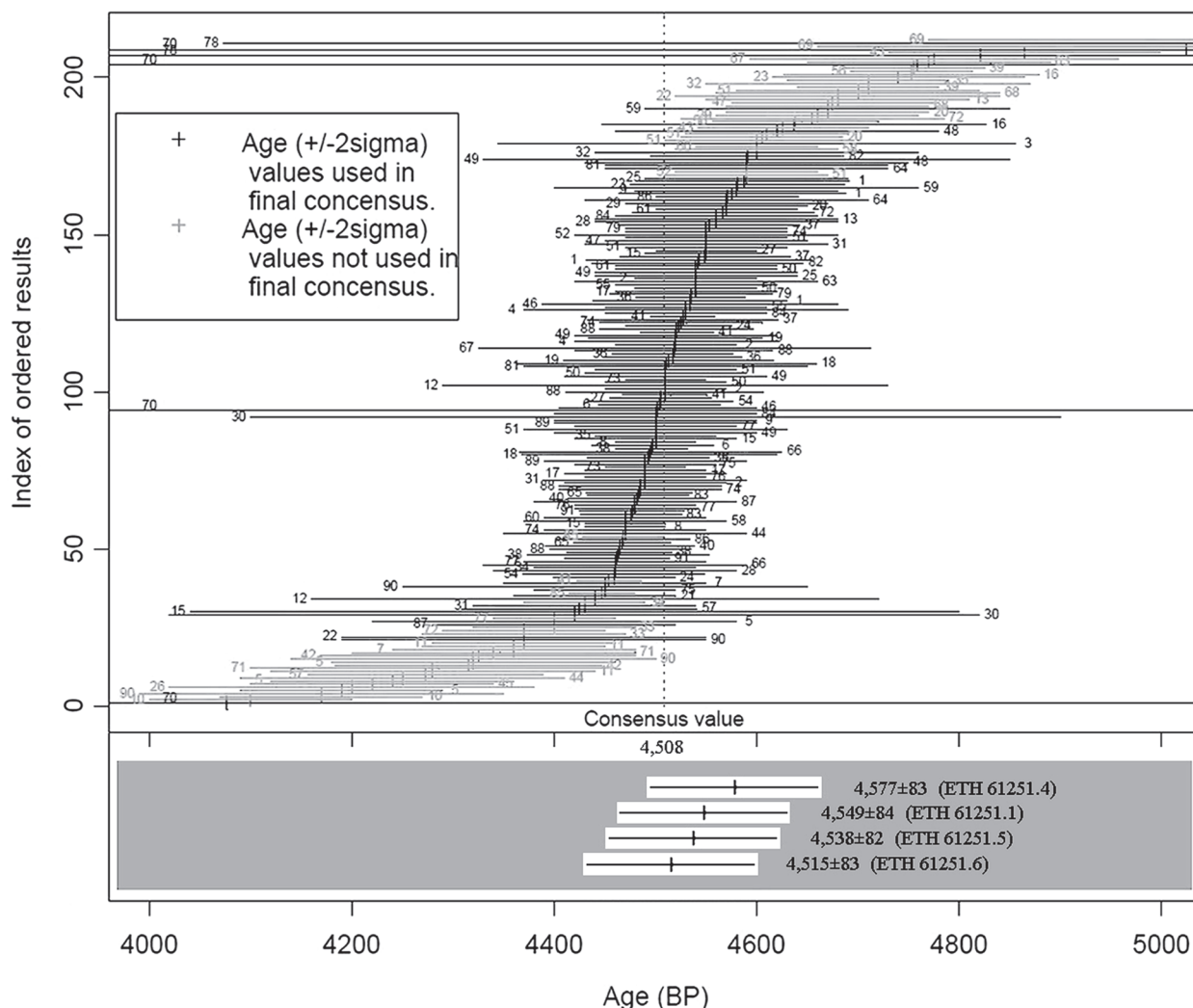
FIGURE 3. AMS DATING RESULTS FOR FOUR NEW MEXICO PLASMA COLLECTIONS FROM THE TIRI BELFAST WOOD STANDARD. THE RESULTS ARE COMPARED WITH THE INTER-LABORATORY COMPARISON RESULTS FOR THE SAME STANDARD FROM THE FIRI STUDY (ADAPTED FROM SCOTT 2003: FIG. 7.3).

Conclusions

Plasma oxidation as a radiocarbon sampling technique began as a novel but relatively narrowly focused idea to deal with the challenges of dating rock art. It has continued to be used for this purpose with dates being produced by three plasma chemical laboratories: Eastern Michigan University (Professor Ruth Armitage), University of Central Arkansas (Professor Karen Steelman), and now the Center for New Mexico Archaeology. At this writing we have dated carbon dioxide samples sent the Zurich ETH AMS laboratory from a pictogram located in Doña Ana County, New Mexico (1972 ± 94 years BP; Dr Lawrence Loendorf) and in the Dominican Republic (1388 ± 84 and 536 ± 82 years BP; Daniel DuVall). Other pictogram samples we have studied have very high background carbon levels in the rock itself,

making dating not feasible (pictograms from Oxtitotlan, Guerrero, Mexico).

Final validation is needed for all techniques for dating rock art as expressed by a quote from the book, *Faust in Copenhagen: a struggle for the soul of physics* by the Nobel Laureate Emilio Segre.

A second opinion was going to be necessary, no matter how reliable … results were. There was always some possibility of error …, and the standard operating procedure for an important experiment was, and still is to have it repeated in another laboratory. If results agree, the community can proceed with confidence.

Until more determinations are made on replicate samples by all different laboratories dating pictograms, using

different techniques and agreement is observed, we cannot consider any technique to be proven.

Acknowledgments

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