A Short Introduction to In Situ Cosmogenic Nuclide Dating

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The in situ cosmogenic nuclide dating techniques, often referred to as 'surface exposure dating' or 'cosmic ray exposure dating', are based on the principle that rare isotopes are produced at Earth's surface through cosmic ray bombardment of elements in surficial rocks and sediments (Gosse & Phillips 2001; Dunai 2010). Over the past three decades, most cosmogenic nuclide applications have been aiming at reconstructing the evolution of landscapes or the formation of geomorphic features, on time scales from a few hundred to a few million years (Schäfer et al. 1999; Schimmelpfennig et al. 2014a). Many of these investigations seek to date simple exposure histories, i.e. to understand since when surfaces have been exposed, e.g. due to glacier retreat, a seismic event or a volcanic eruption (Balco 2011; Benedetti & van der Woerd 2014; Bromley et al. 2019). Other studies have aimed to determine how long deeply shielded sediments were buried, e.g. in a cave. This can be worked out by measuring cosmogenic nuclide concentrations in the sediment if it had been previously exposed (Granger & Muzikar 2001).

The most routinely analysed cosmogenic nuclides are ^{10}Be, ^{26}Al, and ^{36}Cl. The application of in situ ^{14}C, ^{3}He and ^{21}Ne dating is less common, and that of others is still in development (Dunai et al. 2022). Production of all cosmogenic nuclides is based on the following phenomena. Primary cosmic ray particles, originating from supernovae in space and consisting mostly of protons, undergo a cascade of particle reactions once they have penetrated through the geomagnetic field into the Earth's atmosphere. The resulting secondary cosmic ray particles, in particular neutrons and muons, eventually reach Earth's surface, where they interact with target elements, such as oxygen and calcium, in the rock (Figure 1). As a product of these interactions, cosmogenic nuclide concentrations steadily increase in the mineral's crystal lattice as long as the surface is exposed. The exposure age of a surface sample can thus be calculated after analysis of the sample's nuclide concentration and determination of the speed at which the nuclide is produced in the specific sample, the so-called local production rate (Dunai 2010; Gosse & Phillips 2001).

The first step for exposure dating is sampling, which consists of detaching a layer of rock a few centimetres thick from a surface that can be assumed to have experienced undisturbed exposure, i.e. that has not been affected by significant sediment or soil cover or removal of surface material through natural or anthropogenic processes (Dunai 2010). Typical tools used are hammer, chisel and sometimes a purpose-appropriate angle grinder. Once in the laboratory, the rock pieces are crushed, sieved and, depending on the nuclide to be analysed, particular minerals have to be isolated and purified using methods that include magnetic separation and acid leaching (Dunai 2010; Schaefer et al. 2022). The chemical protocols to extract ^{10}Be, ^{26}Al and ^{36}Cl from the rock or mineral phases, developed since the 1980–1990s, consist of three steps: acid dissolution, purification from other elements, and precipitation (Kohl & Nishiizumi 1992; Merchel & Herpers 1999). The final precipitates are eventually analysed by accelerator mass spectrometer (AMS) (Finkel & Suter 1993). The virtues of this specific measurement technique, developed since the 1970–1980s, include but are not limited to the counting of the ultra-low cosmogenic isotope abundance relative to a stable isotope of the same element; e.g. nowadays, measured ^{10}Be abundances are typically 10^{11} to 10^{15} times lower than those of ^{9}Be (Arnold et al. 2010; Rood et al. 2010). The resulting isotope ratios allow for determination of the nuclide concentrations. These concentrations together with site-specific and sample-specific information, necessary to best estimate the local production rate, are then used to calculate the exposure age, by means of appropriate equations or accessible calculators (e.g. Balco et al. 2008; Martin et al. 2017; Schimmelpfennig et al. 2009).

Production rates of the various cosmogenic nuclides are relatively well known, but the global data set is still continuously being complemented and refined (Balco 2020; Martin et al. 2017). Production rate calibrations rely on cosmogenic nuclide measurements in natural surface samples with well-known exposure histories constrained by other dating methods, most commonly radiocarbon dating (e.g. Fenton et al. 2011; Schimmelpfennig et al. 2014b; Young et al. 2013). Production rates vary locally with latitude and altitude due to variations in the strength of the geomagnetic field and the atmospheric depth through which the cosmic ray particles have travelled (sample site elevation) (Dunai 2010). However, calibrations cannot be realized everywhere on Earth. Therefore, local production rates are scaled from calibration sites to other sites of interest using appropriate scaling models, and literature production rate values are, by convention, expressed relative to sea level and high latitudes (e.g. Lifton et al. 2014; Stone 2000).

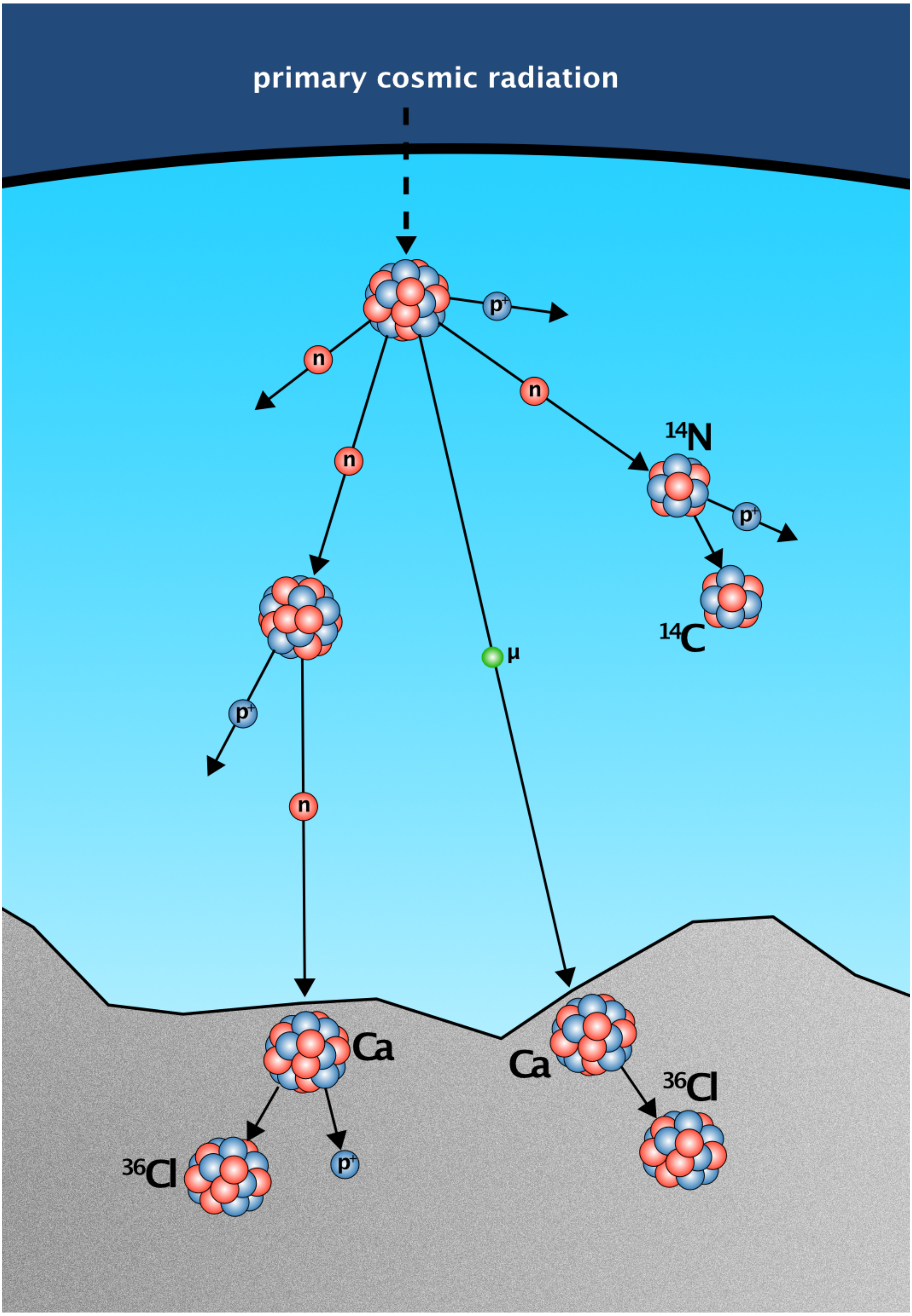

Figure 1. Simplified representation of particle reactions in the atmosphere and in situ cosmogenic chlorine-36 production in surficial limestone induced by secondary neutrons and muons.

The Method's Operational Sequence

Archaeological questions

- To date the closure of the prehistoric porch
- To specify whether the closure was gradual or abrupt, and to assess its impact on access to the cave and on human and animal traffic

Choice of chosen chronometric method

- At the time of the cliff's collapses, the freshly created cliff-faces overhanging the cave entrance began to be ex posed to cosmic radiation
- In situ cosmogenic chlorine-36 steadily accumulates in the fallen limestone blocks' surfaces
- Analyses of chlorine-36 in surface samples provide cosmic ray exposure ages for the rockfall events

Samples

- Sampling of the wall above Chauvet Cave's prehistoric porch
- Choice of samples based on previous geomorphological studies, which had highlighted three zones of collapse
- Sampling needs to take into account constraints imposed by the cultural significance of the cave, i.e. conservation constraints on the archaeological site

Analyses in the laboratory

- Chlorine-36 is chemically extracted from crushed and sieved limestone samples through steps of dissolution in acids and precipitation as silver chloride
- Isotope ratios are measured in the final silver chloride pre cipitates by accelerator mass spectrometer
- The inferred chlorine-36 concentrations and the sample-specific chlorine-36 production rate allow for cal culation of the cosmic ray exposure ages

Results

- Cosmogenic dating (chlorine-36) shows three phases of collapse of the limestone cliff above the cave entrance

Sample identity	^{36}Cl age (ka)*	^{36}Cl weighted mean age (ka)†
1.01	30.2 ± 1.9	**29.4 ± 1.8**
1.02	28.6 ± 1.8	
1.03	24.1 ± 1.5	**23.5 ± 1.2**
2.01	22.6 ± 1.5	
2.02	25.9 ± 1.6	
2.03	25.0 ± 1.6	
2.04	23.3 ± 1.5	
3.01	21.1 ± 1.3	
1.05	19.1 ± 1.3	**21.5 ± 1.0**
1.06	21.4 ± 1.4	
2.05	19.0 ± 1.3	
2.06	21.0 ± 1.4	
2.07	22.5 ± 1.7	
2.08	*14.3 ± 1.1*	
2.09	21.9 ± 1.4	
3.02	23.5 ± 1.6	
3.03	24.8 ± 1.6	
3.04	22.2 ± 1.4	
3.06	21.0 ± 1.3	
4.01	22.0 ± 1.4	

Archaeological implications

- Cosmogenic dating indicates that the closure of the Pleis tocene entrance took place in three stages
- After the first two collapses, the cave entrance could no longer be seen from a distance; it ceased to be a landform that acted as a beacon or visible territorial marker for people in the landscape
- The third collapse closed the cave off completely and thus prohibited all entry into the cave by people and fauna

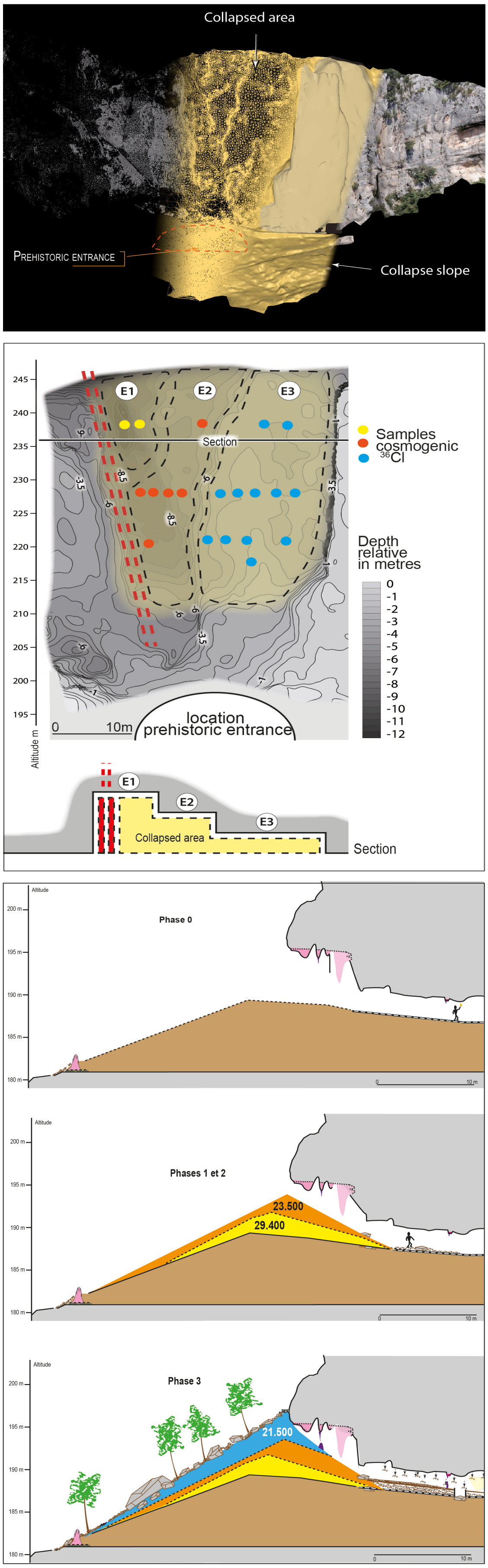

Figure 2. Dating by cosmogenic ^{36}Cl of the obstruction events of Chauvet Cave's entrance

The choice of cosmogenic nuclide for dating a surface sample mainly depends on the lithology and mineralogy of the site of interest. ^{10}Be is produced from the target elements oxygen and silicon and is therefore routinely analysed in quartz (SiO_2) due to the widespread occurrence of quartz-bearing rocks and the relatively simple ^{10}Be extraction procedure (Schaefer et al. 2022). The most important target elements of ^{36}Cl are calcium and potassium, which is why it is the nuclide of choice in carbonate environments (e.g. calcite and limestone $CaCO_3$), various Ca- and K-rich minerals (in particular Ca- and K-feldspars, Ca-pyroxene) and quartz-lacking silicate lithologies such as basalts (Schimmelpfennig et al. 2009, 2011; Stone et al. 1998). ^{26}Al and in situ ^{14}C are analysed in quartz usually in combination with ^{10}Be to investigate complex exposure histories, including burial and/or denudation (Granger and Muzikar 2001; Hippe 2017; Lal 1991). These paired nuclide approaches rely on the different decay rates of these radionuclides (half-lives: $^{10}Be = 1.39 \pm 0.01$ Myr; $^{26}Al = 0.71 \pm 0.02$ Myr; $^{14}C = 5.73 \pm 0.03$ kyr) (Dunai 2010; von Blanckenburg & Willenbring 2014).

Although the potential of applying cosmogenic nuclide dating techniques to archeological research questions has been described and tested over the past few decades, the approach is still rather uncommon in this field (Akçar et al. 2008, 2009; Phillips et al. 1997; Stuart 2001). Theoretically, exposed human-made artefacts, such as monuments or building stones, might be directly dated according to the same simple surface exposure or burial dating approaches as those applied to geomorphic samples. However, the main limitation resides in the fact that the exposure history of the rock material prior to its past processing by humans is unknown. It might have been quarried or collected from surface or near-surface locations and thus have accumulated substantial cosmogenic nuclide concentrations (Akçar et al. 2009; Merchel et al. 2013), also referred to as 'nuclide inheritance'. Instead, cosmogenic dating of geomorphic and geologic features that allow constraining chronologies of human presence or occupations has proven a powerful approach in archaeology. One prominent example, the dating of the rockfall events at Chauvet Cave's entrance, is described in this article (see Sadier et al. 2012). The study takes advantage of the limestone cliff surfaces freshly created and exposed when significant amounts of rock material fell from the vertical walls until the rockfall totally sealed access into the cave (Figure 2). These rockfall events could be dated using cosmogenic ^{36}Cl. Elsewhere, the ages of hominin bones or artefacts were constrained by $^{10}Be/^{26}Al$ burial or exposure dating of the sediments which hold the fossils or artefacts. For example, the remains of a *Homo erectus* cranium in a Turkish travertine quarry were dated to at least 1.1 Ma (Lebatard et al. 2014); the ages of the 'Little Foot' skeleton and stone tools in the cave of Sterkfontein (South Africa) were refined to c. 3.7 Ma and c. 2.2. Ma, respectively (Granger et al. 2015); and a minimum age of c. 620 ka could be determined for stone tools found in an alluvial terrace in the Congo (Braucher et al. 2022).

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