An aminostratigraphy for the Quaternary of the Swiss Plateau

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Highlights

- Amino acid geochronology in a range of biominerals provides the first aminostratigraphy for the Swiss Plateau (lowland Switzerland north of the Alps)
- Intra-crystalline protein decomposition (IcPD) in novel biominerals (slug plates and worm granules) exhibit useful age information
- This aminostratigraphy is coupled with a new molluscan data for the Swiss Plateau from the older Early Pleistocene until the Late Pleistocene

Abstract

Here we develop an amino acid chronology to help establish a dated sequence for the important Early Pleistocene Höhere and Tiefere Deckenschotter lithostratigraphic units, as well as other Quaternary deposits from the Swiss Plateau. Age discrimination is possible between the Quaternary sites from the Swiss Plateau in six different biominerals: *Bithynia* opercula, shell fragments from *Fruticola*, *Arianta* and *Cepaea*, slug plates and worm granules. This chronology is compared with new and existing dating information derived from palaeomagnetic data, pollen, lithostratigraphy and numerical dating methods (such as optically stimulated luminescence; OSL), as well as biostratigraphic data derived from a study of Early to Late Pleistocene molluscan faunas from the Swiss Plateau. In general, the stratigraphy has been validated, with some new chronological insights at some of the few sites.

1. Introduction

The Alpine Foreland region is especially propitious for the study of Pleistocene litho- bio- and climatostratigraphy due to the survival of both glacial and interglacial deposits. This explains why the worlds first ever regional stratigraphy was attempted by Penck and Brückner (1901-1909) for the Alpine Foreland of southern Germany, when they named four glacial periods (Günz, Mindel, Riss and

Würm). Subsequent studies have shown, however, that the Quaternary glacial history in the Alpine Foreland area is much more complex and that significantly more glaciations have left their imprint on the landscape (Graf, 1993; Doppler *et al*., 2011; Ellwanger *et al*., 2011; Preusser *et al*., 2011; van Husen & Reitner, 2011; Schlüchter *et al*., 2021). One of the outstanding problems that confronts any attempt at establishing a detailed regional chronology is the need to produce relative and absolute dates for the surviving deposits, which tend to be spatially separated and fragmentary due to the destructive effects of successive glacial advances. The existing chronology for the Pleistocene in Switzerland, for example, has many gaps and unknowns, especially for the Early and early Middle Pleistocene (Schlüchter *et al*., 2021). Similar problems exist for the chronologies of southern Germany and Austria (Doppler *et al*., 2011; Ellwanger *et al*., 2011), in particular for the Early and early Middle Pleistocene, which hamper a greater understanding of glacial and interglacial histories for the wider Alpine region.

The Quaternary archive of northern Switzerland has long been morphostratigraphically divided into four units, with the highest being considered to be the oldest: the Höhere Deckenschotter (HDS; Higher Cover Gravels), Tiefere Deckenschotter (TDS; Lower Cover Gravels), Hochterrasse (Higher Terrace) and Niederterrasse (Lower Terrace). 'Deckenschotter' units refer to mostly fluvioglacial gravels that form a more or less horizontal covering to low, plateau-like hills. The two Deckenschotter units documented from northern Switzerland are separated by an important phase of incision. Four similar morphostratigraphic units were originally defined for the Alpine Foreland of southern Germany by Penck and Brückner (1901-1909), who correlated them with their four named glacial periods (Günz, Mindel, Riss and Würm). Despite more recent work that has established that the deposits of up to 16 glaciations are recorded in northern Switzerland, of which four have been linked with the formation of the HDS (Graf, 2009, Preusser *et al*., 2011), a modified version of the four morphostratigraphic units is still used in northern Switzerland (Graf and Burkhalter, 2016).

The formation of the terrace levels has been explained by progressive fluvial incision, with higher level terraces thought to reflect older regional base-levels, while lower terraces represent subsequent younger regional base-levels. The situation within areas influenced by glacial advances is complex however, as later ice advances can erode and alter previous sedimentary archives. This is the case for much of the Alpine and Upper Rhine system of northern Switzerland, where local terrace levels do not necessarily reflect regional base-levels, because a terrace level can reflect deposition linked with a local glacier advance, and therefore be at a higher level than the regional or previous interglacial base-levels. In such a setting, determining depositional ages and the correlation of sedimentary successions is essential for understanding this fragmentary and complex sedimentary archive. Fluvial incision rates, for example, can be estimated from the elevations and ages of terraces. These can in turn be important for establishing the rates of various linked processes, such as the long-term uplift of the Alps, which may be a major forcing agent for fluvial incision.

The sediments of the four morphostratigraphic units are mostly composed of thick fluvioglacial gravels and sands that are difficult to date. In deposits older than the last glacial Niederterrasse, fine-grained deposits are uncommon and silty layers with preserved biological material are even rarer. Relatively few studies have dated sediments older than the last glaciation, with techniques including luminescence dating, cosmogenic radionuclide dating, magnetostratigraphy and biostratigraphy (Table 1 and references therein). Some recent investigations using luminescence and cosmogenic dating suggest that previously proposed ages and correlations may have to be reconsidered (e.g. Gegg *et al*., 2022; Dieleman *et al*., 2022a). Additional independent evidence for the timing of depositional archives is therefore needed to improve current understanding of Quaternary landscape evolution.

When Pleistocene deposits contain biomineral remains such as mollusc shells, then there is also the potential to develop an aminostratigraphy for the region, using the extent of protein breakdown in certain biominerals (e.g. Abelson, 1955; Miller and Mangerud, 1985; Wehmiller *et al*., 2021). In this study the relative timing of several key archives from the Swiss Plateau is investigated for the first time using an aminostratigraphy of calcium carbonate biominerals. Molluscs have long been known to have biostratigraphical importance in Quaternary deposits due to the appearance and disappearance of certain marker species (cf. Meijer, 1986). Molluscs were known from Middle Pleistocene Hochterrasse and Late Pleistocene Niederterrasse deposits in northern and central Switzerland linked with the Rhine system, but due to an absence of recent work, identifications were incomplete and in many cases in need of revision (Thew, 2024). Similarly, molluscs from Middle and Late Pleistocene sites from the southern part of the Swiss Plateau (linked with the Rhône system) have also been re-examined to complete the picture (Thew, 2024).

Previous studies have shown that the intra-crystalline fraction of *Bithynia* opercula exhibits closed-system behaviour (Penkman *et al*., 2011; Tesakov *et al*., 2020), so its presence in a small number of the Swiss deposits made it an obvious target for aminostratigraphy. Where closed-system behaviour is evident, then protein decomposition should depend solely on time and temperature (e.g. Brooks *et al*., 1990; Penkman *et al*., 2011), so within a region that has experienced the same integrated temperature history (Miller *et al*., 1999; Wehmiller *et al*., 2000), the extent of IcPD provides a relative chronology. In addition, various other biominerals (aragonitic *Arianta*, *Cepaea* and *Fruticola* mollusc shells, plus calcitic slug plates and worm granules), were present across a wider range of sites and horizons, and so this study aimed to test their potential for amino acid geochronology. Chiral amino acid analyses were undertaken on bleached samples to determine the intra-crystalline protein decomposition (IcPD) behaviour in these biominerals. The IcPD in this combination of biominerals was then used to develop the first aminostratigraphies for this region of central Europe, providing a relative chronology for several key archives from the Swiss Plateau.

2. Materials and Method

2.1. Material selection

Mollusc shells were first discovered in deckenschotter deposits in northern Switzerland by Frei around 1910 (Frei, 1912), with 10 terrestrial species recovered from silty lenses in a sequence of HDS gravels at Eichbrunnen, near Freienwil, at the foot of the Dürn-Gländ Plateau (AG). More recently, shells were discovered in 1955 by Bräm (Bräm, 1956) in a unit of silts and fine sands within a sequence of HDS gravels at the Irchel Plateau (ZH). Subsequent investigations at the same locality by Graf in 1990-92 (Graf, 1993, p.35-48) and by Bolliger *et al*. in 1994-95 (Bolliger *et al*., 1996) confirmed the frequent presence of mollusc shells at Irchel, with 14 terrestrial species plus 4 genera and 1 aquatic taxon identified. Since then, shells have also been found in fine layers within fluvial gravels at the base of a HDS terrace at Albishorn-Bürglen (Graf, 2019, p.9) and within silty alluvial deposits at the base of a TDS sequence at Hungerbol, near Schienen (Baden-Wurtemburg; Graf, 2009, p.23-25).

2.2. Site selection

An extensive survey was carried out to identify sites with suitable biominerals such as mollusc shells, which would allow an aminostratigraphic framework to be developed for the Swiss Plateau. Firstly, a literature study was conducted that focused on the HDS and TDS deposits in northern Switzerland, although Hochterrasse sites were also considered. This process greatly benefited from pre-existing studies (such as Graf, 1993, 2009, 2019) and the explanatory notes that accompany the 1:25,000 maps of the Geological Atlas of Switzerland. As a second step, localities from northern Switzerland were assessed in the field, with still accessible sites that had previously shown a high potential being selected for re-sampling and analysis. Thirdly, the collections of the Natural History Museums in Basel, Bern and Geneva, the Paleontological Museum of the University of Zürich, the ETHZ in Zürich and the Cantonal Museum of Geology in Lausanne were checked for suitable molluscan assemblages and/or unprocessed sediments from sites across the Swiss Plateau. Specialists likely to have amassed suitable shell material and/or sample sediments were also contacted. Finally, molluscs from sites that had been previously studied (by NT) and had independent dating evidence (such as Niederweningen, Abri Unterkobel and Oberbipp) were also considered.

It transpired that deposits with preserved mollusc shells are extremely rare in HDS and TDS sequences in northern Switzerland and neighbouring areas of southern Germany. For the TDS, for example, the only locality where suitable material could be recovered was Hungerbol, in south-western Germany. Most Middle and Late Pleistocene material, by contrast, has been obtained from previously collected archival samples. In all, biomineral material has been studied from deposits that cover much of the Quaternary, from HDS and TDS through Hochterrasse and the Niederterrasse into the Holocene, incorporating many key interglacial and interstadial mollusc-bearing sites from across the Swiss Plateau (Table 1). Detailed site information is reported in the relevant references, while the key points are summarised here.

2.2.1. *Early Pleistocene*

2.2.1.1. Irchel Plateau (Ebni, Hasli [Bräm, 1994/95, 2018/19], Steig, Amselboden, Hochwacht)

The Irchel Plateau is located in north-eastern Switzerland, close to the border with Germany. It is a low hill of molassic sandstone capped by HDS deposits. The HDS sequence includes a series of four units of massively bedded, fluvioglacial, braided-type gravels interrupted by two levels of silty deposits with preserved biological material. The lower level, below the fluvioglacial Irchel Gravel at Ebni (Graf, 1993; Preusser *et al.*, 2011, Thew *et al.*, 2024), consists of up to 2.5 m of fine sands and silts consistent with warm period flood plain deposits with biological material including molluscs (NEaar 13281-3), ostracods, *Chara* and earthworm granules (NEaar 13333-7).

Above the Irchel Gravel and Steig Gravel (Graf, 1993; Preusser *et al.*, 2011), the Hasli Formation (HF) comprises up to 6.2 m of river floodplain silts and fine sands, with abundant well preserved biological material that includes small mammal teeth, molluscs (Thew *et al.*, 2024; NEaar 13116-21; 13229-34; 13284-93), earthworm granules (NEaar 13315-20; 13330-2; 13338-40). At Hochwacht and Amselboden (NEaar 14025-30; 14144-6), the base of the HF is notably coarser, with sand and fine gravel, and includes rare fragments of *Bithynia* opercula (NEaar 14141-2; 14147-8).

The molluscan faunas of the HF include 20 species never before been seen in Swiss Quaternary deposits, several of which are extinct. Most of these have modern or palaeo distributions that lie far to the west, south and east of the Swiss Plateau, indicating that the climate was significantly warmer than today, with hotter summers and milder winters (Thew *et al.*, 2024), in keeping with elevated global surface palaeotemperature reconstructions for this period (Snyder, 2016, Fig.1). The small mammal assemblage from the upper part of the HF at Irchel Hasli suggests a date from 2.0 to 1.8 Ma for the upper part of the HF (Thew *et al.*, 2024). This evidence is consistent with the molluscan biostratigraphy, as there are several species that became extinct at the end of the Tiglian warm stage at 1.76 Ma (Thew *et al.*, 2024, Thew, 2024). Also of note is the probable presence of *Fagus* pollen at both Hasli and Hochwacht, which became rare after the Tiglian for the rest of the Early Pleistocene (Graf, 1993, p.46; Bludau, 1995; Hahne *et al.*, 2008, Thew *et al.*, 2024). The lower part of the HF has a palaeomagnetic signal with reversed polarity, while the upper levels have normal polarity (Scheidt *et al*., 2023). Based solely on palaeomagnetic data, this change might correspond to the start of either the Olduvai Subchron or the Jaramillo Subchron, but when the small mammal and molluscan data is taken into account, this palaeomagnetic transition clearly marks the beginning g of the Olduvai subchron, which took place at1.934 Ma (Ogg, 2020; Raffi *et al*. 2020).

At Hochwacht, the HF is succeeded by up to 4.2 m of bedded fluvial gravels, which c.3 m above the HF include silty soft clasts and a large lens of silty fine sand (2.5 m across by up to 0.4 m thick). Both contain rich molluscan faunas typical of warm interglacial conditions and a densely forested floodplain environment (Thew *et al*., 2024; NEaar 13220-2; 14019-21; 14086-8; 14135-14142; worm granules: 13307-8). The molluscan faunas from this 'upper level' are very similar to those of the HF and have the same major biostratigraphic markers, as well as several new species, indicating that this fauna is of a very similar age although it is slightly younger.

The combined evidence shows that the start of the Olduvai subchron at 1.934 Ma seems to have occurred during the upper part of the HF, while the molluscs and small mammals show that both the HF and the 'upper level' with biological remains at Hochwacht West belong to the same biostratigraphical period before the end of the Tiglian at 1.76 Ma. A continuity of the molluscan evidence throughout the HF indicates that there were no major biostratigraphic hiatuses. If it can be assumed that sedimentary accumulation was fairly constant from the start of the Olduvai subchron until the end of the HF (at around or not long before 1.8 Ma), extrapolating rates of sedimentation for the lower part of the sequence before the palaeomagnetic transition seems to imply that the HF probably began to accumulate before 2.0 Ma. The most accurate age estimate for the HF may therefore be 2.1-1.8 Ma, with the 'upper level' dating from c.1.8 Ma (Thew *et al*., 2024).

The stratigraphic position of the 'Ebni silts' beneath the Irchel Gravel suggests that they predate the HF and are thus of a pre-Olduvai age (Thew *et al*., 2024). As the 'Ebni silts' seem to coincide with an event of normal polarity, it is possible that they may correspond to a rare recording of the Feni (Réunion) Subchron, which is dated to 2.155-2.120 Ma (Fig. 13b; Raffi *et al*. 2020).

The gravels of the Irchel Plateau below the HF have also been investigated by cosmogenic dating techniques (Claude *et al*., 2019; Dieleman *et al*., 2022a). Some of the ages they have produced differ from the age for the HF proposed above based on biostratigraphy, palaeomagnetic data and the lithostratigraphic concept of Graf (1993). For example, at Steig and Hasli the Steig Gravel below the HF has been dated by the isochron-burial method to 0.9 ± 0.4 and 1.3 ± 0.1 Ma, while the Irchel Gravel below the Hasli Formation at Hütz and Hochwacht has isochron burial dates of 0.9 ± 0.4 and 2.6 ± 0.1 Ma (Dielemann *et al*., 2022a). Based solely on the cosmogenic ages, additional gravel-filled channels that cross-cut across the Irchel Plateau have been proposed to explain the apparent age contradictions, but so far no filed evidence has been produced to verify these, and extensive clast petrographic data seems to confirm Graf model (Thew *et al*., 2024).

2.2.1.2. Albishorn-Bürglen 2

This site is located near the eastern margin of Lake Zürich in north-eastern Switzerland. The molluscs come from several layers of sand and sandy-silt present within up to 17 m of fluvial gravels known as the Albisboden Gravel, which form the lower part of a sequence of HDS deposits. The molluscs include most of the important biostratigraphic marker species present in the Hasli Formation at Irchel, with the presence of the marker species *Clausilia stranzendorfensis* and *Cochlostoma salomoni* suggesting an age before 1.8 Ma (Thew, 2024), while the comparable faunal association may indicate that deposition was more or less contemporary with the Hasli Formation. The basal part of the gravels, from which the worm granules (NEaar 13347-9) and *Bithynia* opercula are from (NEaar 14613), has reversed palaeomagnetic polarity (Graf, 2019). The polarity of the fine layers from the upper part of the gravels, from which the slug plates (NEaar 14615-7) derive, has not been studied.

2.2.1.3. Albishorn-Bürglen 1

Above the thick fluvial gravels of Albishorn-Bürglen 2 (Albisboden Gravel) are 2-6 m of fluvioglacial gravels with large boulders, followed by 9-12 m of compact ground moraine (Bürglen Till) (Gubler pers. com.). Then, within the upper part of the same HDS sequence are up to 1.4 m of grey-brown fairly organic sandy-silts/silts with bands of dark blackish-brown lignite and grey tufaceous silt that represent Albishorn-Bürglen 1. The molluscs include a significant number of interglacial species, showing that the silts of Albishorn-Bürglen 1 represent a second warm interglacial period within this HDS sequence, including small fragments of *Bithynia* operculae (NEaar 14614). There was thus an important stratigraphic break after the warm period represented by the gravels of Albishorn-Bürglen 2 (see above), when a major advance by the Linth-Rhine Glacier led to the formation of the fluvioglacial gravels and basal moraine. Then, after the interglacial period represented by the silts of Albishorn-Bürglen 1, a second glacial advance led to the deposition of another thick glaciogenic unit. The Albishorn-Bürglen 2 gravels seem to represent the first or second of the three sub-units that Graf has defined for the HDS in northern Switzerland (Graf, 2019, fig.16, p.21-23), while the succeeding deposits, including the Albishorn-Bürglen 1 silts, belong to the third sub-unit of the HDS.

The Albishorn-Bürglen 1 faunas include few of the biostratigraphical markers present at Albishorn-Bürglen 2 and the Irchel sites, but instead have four new marker species (*Cochlodina fimbriata*, *Macrogastra attenuata*, *M. plicatula*, *Monachoides incarnatus*), the first two of which have never been found in Tiglian deposits (Thew, 2024). This evidence indicates that the molluscs from Albishorn-Bürglen 1 are significantly younger than the faunas of Albishorn-Bürglen 2 and are probably post-Tiglian.

Similarly, although a pollen sequence through the same organic silts includes several thermophilous tree species typical of a warm interglacial, there is no sign of *Fagus* despite thousands of pollen grains being counted. *Fagus* pollen is rather common in older Early Pleistocene contexts, but is rare in deposits dating from the middle and later Early Pleistocene (Bludau, 1995; Hahne *et al*., 2008). As *Fagus* has been found in the Hasli Formation at Hasli and Hochwacht, this indicates that the Albishorn-Bürglen 1 silts are notably younger and are probably post-Tiglian.

Just after the end of the Olduvai Subchron (at 1.78 Ma, there was a notable cooling that marks the transition from the Tiglian warm stage to the Eburonian cold stage in the North-West European Chronology and denotes the transition from the older Early Pleistocene to the middle Early Pleistocene. The cooling coincided with important faunal transformations in both terrestrial and oceanic sequences (Cohen and Gibbard, 2022), including the extinction of several key mammalian and molluscan biostratigraphic marker species. The middle Early Pleistocene incorporates two stages in the North-West European Chronology: the Eburonian cold stage from 1.76-1.49 Ma, and the Waalian warm stage from 1.49-1.22 Ma. During the Eburonian there is clear evidence for significant glacial activity in Europe, while there appears to have been minimal glacial activity in lowland areas during the Waalian. It therefore seems more likely that the glacial advances represented by the Bürglen Till and the Albiswald Gravel-Till occurred during the Eburonian. If true, then the interglacial silts of Albishorn-Bürglen 1 would be the first site known from Switzerland with biological material dating from the middle Early Pleistocene.

2.2.1.4. Hungerbol, D

Hungerbol is located just inside south-western Germany, near the NW corner of Lake Constance, within a low-lying hill capped by Quaternary sediments called the Schiener Berg. These deposits represent the morphostratigraphic unit known as the Tiefere Deckenschotter (TDS), which like the HDS is found in northern Switzerland and neighbouring areas of south-western Germany (Graf, 2009; Preusser *et al*., 2011). In the traditional model, the TDS is lower than the HDS, so should be younger, meaning that Hungerbol is stratigraphically younger than Albishorn-Bürglen 1. At the base of the Hungerbol sequence are 1 to 4 m of finely bedded fluvial gravels and sands, which are succeeded by up to 2.8 m of silts and fine sands with biological material that represent Hungerbol 2 (NEaar 12244-50, 13327-9; 14618-9). After 0.8 m of sterile fluvial gravels there are up to 2.2 m of silts and fine sands with mollusc shells that represent Hungerbol 1 (NEaar 13131-3, 13324-6). All of these sediments seem to have been deposited by the same meandering river, but while Hungerbol 2 has a fauna typical of warm interglacial conditions and a floodplain environment with fairly dense, largely deciduous forest, the molluscs of Hungerbol 1 seem to represent a mild interstadial within the early part of the succeeding cold period. The sequence is completed by over 5 m of fluvioglacial gravels linked with a nearby ice front (Graf, 2009a, p.23-25). The sequence within the Schiener Berg is completed by up to 50 m of basal till, followed by another c.15 m of fluvioglacial gravel, and then a further fluvioglacial unit at a somewhat lower level.

The small mammal remains recovered suggest that Hungerbol 2 dates from between 1.8/1.7 and 1.1/1.0 Ma (Maul & Markova, 2007). The molluscan faunas appear to belong within the Early Pleistocene due to the continued presence of eastern species like *Monachoides vicinus* that seem to have disappeared from the Swiss Plateau after the later Early Middle Pleistocene, and an absence of marker taxa for the Middle Pleistocene (Thew, 2024). The faunas are fairly similar to those of Albishorn-Bürglen 1, but have two additional biostratigraphic marker taxa, *Clausilia cruciata* and *Platyla polita*. The fauna also suggests that the climate is likely to have been either similar or slightly warmer than that of today. Given the paucity of evidence for glaciations in lowland Central Europe of glacial deposits from the period known as the Waalian warm stage, that lasted from 1.49-1.22 Ma, it seems possible that the glaciogenic and fluvioglacial deposits that succeed the Hungerbol 2 and Hungerbol 1 silts, as well as the silts themselves, date from after 1.22 Ma, during the later Early Pleistocene (cf. Head and Gibbard, 2015).

2.2.2. Middle Pleistocene

The choice of sites with molluscan material that dates from the Middle and Late Pleistocene was largely governed by what was available in museum collections, although every effort has been made to have shells from as broad a temporal range as possible, as well as having sites that were spread across the Swiss Plateau.

2.2.2.1. Ecoteaux

Ecoteaux is a small palaeo lake basin located in south-western Switzerland near the foot of the Alps (Pugin *et al*., 1993). Above the Tertiary Molasse, there are glacial deposits associated with reversed palaeomagnetic polarity (thus likely to be late Early Pleistocene), followed after a hiatus by glacial deposits associated with normal palaeomagnetic polarity (that are Middle Pleistocene), then 11.5 m of laminated organic sandy-silts (Layer 7), followed by 5.5 m of silty-sands, with some gravel in the basal 1.3 m (Layer 8), with Layers 7 and 8 having wood fragments, plant remains and mollusc shells. After another hiatus, the sequence terminates with LGM basal till. The analysed molluscs (where IcPD analyses were undertaken, NEaar 13110-2) were sampled in nearby surface exposures that have been correlated with Layer 7 in the core sequence by pollen analysis (Pugin *et al*., 1993).

The pollen shows that the lacustrine silts of Layers 7 and 8 correspond to two interglacial periods separated by a colder interval, although the continuation of low frequencies of *Taxus*, *Abies* and *Corylus* indicates that conditions were never truly cold (Pugin *et al*., 1993). Both interglacials have low frequencies of *Pterocarya*, but more importantly the earlier interglacial has up to 2% *Carya*, which became rare in most of Europe after the Early Pleistocene and disappeared from Europe north of the Alps by the end of Cromerian (end of marine oxygen isotope stage (MIS) 13; Hahne *et al*., 2008; Orain *et al*., 2013; Magri *et al*., 2017). This suggests that both warm periods correspond to the early Middle Pleistocene, as postulated by Schlüchter (2017; Schlüchter *et al*., 2021). As the molluscs come from the lower of the two interglacials, this might suggest that this mostly aquatic assemblage dates from MIS 15.

2.2.2.2. Montfleury and Sous-Terre 2

Montfleury is located to the west of Geneva, c.1.4 km to the NW of the present course of the Rhône. Two cores: Montfleury 1 (1946 - Lanterno *et al*., 1981) and Montfleury 2 (1981/82 - Wegmüller *et al*., 1995) were taken 115 m apart, with the molluscs coming from Montfleury 1. Above the Molasse, the combined sequence from the two cores comprises: ~30 m of glaciogenic deposits (basal till, fluvioglacial, glaciolacustrine), indicative of full glacial conditions, followed by 1 to 1.5 m of sandy gravel, likely to be late glacial. Then comes up to 8 m of silty sediments with plant remains, mollusc shells (including the NEaar samples 12263-5) and pollen typical of a warm interglacial, termed the ‘Confignon Sequence’ by Wegmüller *et al*. (1995). This is followed by more sandy sediments with mollusc shells in places, called the ‘Vernier Sequence’ by Wegmüller *et al*. (1995). Above this are silty-sands with biological material typical of a warm interglacial, called the ‘Montfleury Sequence’ by Wegmüller *et al*. (1995). After a hiatus, there are thick fluvioglacial gravels (the ‘alluvion ancienne’), then another hiatus succeeded by last glacial maximum (LGM) basal till.

Sous-Terre is located on the right bank of the Rhône, 5 km ESE of Montfleury and 0.5 km from where the river exits Lake Geneva. The sequence begins with a thick deposit of basal moraine (up to 35 m) indicative of full glacial conditions. Above this are 1 to 2 m of grey sandy-silts capped by a thin sandy lignite, with wood fragments, plant material, pollen indicative of a warm interglacial and a rich molluscan fauna (Jayet and Amberger, 1969; ST2, the lower level of IcPD samples, NEaar 12266-8, 13134-6, 13235-7, 13303-5, 13344-6). Above this lie 1.5 to 4 m of very compact laminated blue-grey silts with some plant material (only *Picea* needles), pollen and rare molluscs, indicative of cooler conditions. Above a hiatus are up to 25 m of partially cemented fluvioglacial gravels with erratic blocks, known as the ‘alluvion ancienne’, interpreted as a full glacial. After another hiatus comes LGM basal till, then 0.7 m of grey marly silty-sand with stones and mollusc shells (ST1, the upper level of IcPD samples, NEaar 12260-2), that is early Holocene (discussed in section 2.2.4.1). Above this lies 1 m of late Holocene tufaceous sandy-silt with molluscs and small tile fragments, capped by a modern soil.

The molluscs from both the ‘Confignon Sequence’ at Montfleury and the lower level at Sous-Terre come from sandy-silt deposits linked with an active channel, almost certainly the Rhône, with Montfleury appearing to represent the edge of the palaeo-channel and Sous-Terre a channel margin/floodplain location. The pollen (Hofmann-Grobéty, in Jayet and Amberger, 1969; Girard, 1970; Wegmüller *et al*., 1995), plant macros and molluscs from these deposits are typical of warm interglacial conditions. The pollen and molluscs from the ‘Vernier Sequence’ at Montfleury and from the compact blue-grey silts at Sous-Terre suggest considerably cooler conditions (Reynaud, 1982 p.29; Wegmüller *et al*., 1995).

The pollen suggests that both of these interglacial sediments date from the later Middle Pleistocene. Montfleury has the molluscan marker species *Perforatella bidentata* that disappeared from

Switzerland before the end of the Middle Pleistocene. This species is missing from the fauna from the lower level at Sous-Terre, which instead includes the biostratigraphic markers *A. klemmi* and *Z. sepultus* which both became extinct after MIS 9, while *C. rugosa antiquitatis* seems to have disappeared after MIS 11 (Thew, 2024). The thick glacial deposits that underlie both sites may well represent the 'Möhlin Glaciation,' which seems to have been the most extensive in the Swiss Alpine foreland (Preusser *et al*., 2011). The glacial deposits (Bünten Till) at Möhlin might represent MIS 12 (Dieleman *et al*., 2022b), but this age is disputed (Norgaard *et al*., 2023). This period also saw a major increase in the quantity and coarseness of debris supply into the Upper Rhine Graben north of Basel (Preusser *et al*., 2021).

Taken together, this evidence suggests that the material selected from the interglacial deposits at Sous-Terre and Montfleury are likely to represent MIS 11, which would mean the succeeding cooler deposits correspond to MIS 10.

2.2.2.3. Nuolen/Buechberg

The Nuolen/Buechberg site is located in north-eastern Switzerland near the foot of the Alps and comprises thick gravel sequences corresponding to the Hochterrasse, with intercalated layers of marly-silt, silt and lignite. There are three levels with these fine deposits, but only the Middle Level has been analysed, with Nuolen 1 (NEaar samples 13107-9) coming from the eastern gravel quarry (Swiss Map reference 2710 370/1228 440), while Nuolen 3 (NEaar samples 13128-30, 13226-8, 13309-11) comes from the western gravel quarry (2710 160/1228 620). A lithostratigraphic study of the southern part of the Buechberg by Schindler (2004, p.13-31), has shown that the major stratigraphic units can be traced across most of this area, meaning that correlations between gravel pits are plausible.

The molluscan assemblage from Nuolen 1 represents the margin of a modest palaeo-channel, while Nuolen 3 represents a marshy depression within the floodplain of a smallish river, adjoined by fairly dense, mature, largely deciduous woodland. The molluscan assemblages include the biostratigraphic marker *Urticicola umbrosus*, which disappeared from Central Europe before the end of the Middle Pleistocene (Thew, 2024), while some interglacial species regularly associated with the Eemian, like *Helicodonta obvoluta*, are missing. Pollen analysis by Welten (1988, Diag.12, plus Diags. 8-11) on several profiles from nearby gravel quarries has attributed the 'lower' and middle' levels of marly-silt and lignite to his 'Holstein 1' and the 'upper' level to 'Holstein 2' in the Meikirch sequence. Preusser *et al*. (2005) dated Miekirch 1 and 2 by OSL to MIS 7e and 7c. The molluscan assemblages at Nuolen correspond to the lower of these two warm phases, so may date from MIS 7e.

2.2.2.4. Grandson

Grandson is located in south-western Switzerland, at the western edge of the Swiss Plateau. Samples were taken between 1942 and 1944 in a lignite mine located within a high lake terrace near the south-western corner of Lake Neuchâtel. The sequence consists of three layers of lignite alternating with marly lake silts. The molluscan faunas suggest lake-levels around 50 m above today's level of 429 m asl. The shells analysed for IcPD (NEaar samples 12269-73) come from marly-silts between the lower and middle lignite layers. The lacustrine sediments were covered by up to 12 m of undated fluvioglacial gravels, then by LGM basal till.

The molluscs show that the sampled sediments were deposited during a warm interglacial in a large lake with significant wave action, likely to have been an earlier manifestation of Lake Neuchâtel. Pollen analysis on a core taken 50-100 m to the north-west in 1982 (Welten, 1988, diag.13; Jordi, 1996, fig.7) shows that the sampled sediments correspond to Welten's 'Holstein 1' (presence of *Pterocarya*; Welten 1988), which shows close similarities to the Meikirch 1 that has been dated by

OSL to MIS 7e (Preusser *et al*., 2005). The evidence therefore suggests that the molluscs correspond to MIS 7e.

2.2.2.5. Petit Saconnex and World Health Organisation (WHO), Geneva

Both these sites are located within the city of Geneva, to the west of Lake Geneva, around 2 and 3 km to the north of Sous-Terre, respectively. Above the Molasse, the Petit Saconnex sequence comprises up to 6 m of compact basal moraine indicative of full glacial conditions, then a hiatus followed by up to 9 m of grey interstratified silts and sandy-silts with molluscs and plant remains, then another hiatus succeeded by up to 8 m of partially cemented fluvioglacial sandy gravel ('alluvion ancienne'), then a final hiatus followed by LGM basal till. Of the two profiles at Petit Saconnex, the first was sampled by A. Jayet in 1961 (Jayet *et al*., 1961) but the samples were not re-examined; the second by C. Ruchat in 1994 (NEaar samples 14016-8; 14074-6). These two profiles lie 0.8 to 1.2 km to the south of the site at WHO, where in a core taken in 1979 the molluscs (NEaar 14013-5; 14083-5) come from comparable silts with wood fragments covered by LGM basal till.

The molluscan faunas from the two sites are very similar and pollen and plant macros are typical of an interstadial from the earlier part of a glacial period. The silts from the two sites seem to be contemporary.

The fluvioglacial gravels of the 'alluvion ancienne' that cover the mollusc-bearing silts at Petit Saconnex, as well as the interglacial levels at Sous-Terre and Montfleury, are notably thick in the Geneva area (up to 50 m in places) and have striated clasts, intercalated layers of moraine and erratic blocks, which show that they accumulated near an ice front during a full glacial. They may well date from MIS 6, as this was one of the most extensive of the Middle Pleistocene glaciations in Switzerland (Preusser *et al*., 2011); there is ample evidence that the Rhône Glacier was present in the Geneva area during this period (Coutterand, 2018), and there is a major erosional hiatus linked with the partial or complete removal of these gravels before the deposition of a series of glaciogenic deposits up to 80 m thick in the Geneva area during the last glacial (Moscariello *et al*., 1998). The basal till beneath the silts at both Petit Saconnex and WHO seems to be the same deposit that underlies the sites at Sous-Terre and Montfleury, which is known as the 'Moraine basale inférieure' and is fairly widely present in the Geneva area (Moscariello *et al*., 1998, fig.2). There may have been a major episode of erosion before the deposition of the silts at Petit Saconnex and WHO that removed earlier sediments such as those found at Sous-Terre, Montfleury and Confignon. If true, this might suggest that the silts at Petit Saconnex and WHO may date from the early part of MIS 6, prior to the accumulation of the MIS 6 'alluvion ancienne', although an MIS 8 date for these silts is also possible.

2.2.3. Late Pleistocene

The Late Pleistocene sites at Niederweningen, Zell and Thalgut have deposits that seem to have accumulated during the last interglacial.

2.2.3.1. Niederweningen

Niederweningen is located in the Wehntal Valley, in the north-eastern part of Switzerland, north of Zürich. Studies of deep cores have shown that the lower infill of the valley consists of glaciolacustrine and lacustrine silts that are dated by OSL to MIS 6 (Anselmetti *et al*., 2010; Dehnert *et al*., 2012). After a hiatus, these are succeeded by the thick Lower Peat Complex, which based on the pollen data and the stratigraphy was attributed with the final part of the Eemian (MIS 5e), while its upper part belongs to the Early Würm (MIS 5d to 5a; Welten, 1988). This is followed by alternating silts and thin peaty layers dated by OSL to MIS 4 and the start of MIS 3, which are succeeded by the Upper Peat complex that contains mammoth bones and has been dated by ^{14}C and

OSL to the early-mid part of MIS 3 (Furrer *et al*., 2007; Hajdas *et al*., 2007; Preusser and Degering, 2007).

In 2015 a deposit of tufaceous silts with abundant mollusc shells was discovered in construction trenches for houses near the edge of the valley, to the west of the village centre and the zone where the mammoth bones have been found. Coring in 2018 also located these deposits and confirmed that they are situated above the silts dating from MIS 6 and below the base of the Lower Peat, suggesting that they are probably Eemian. Beneath the tufaceous silts is a thin layer of blue-grey marly silts that also have frequent shell material. Neither the blue-grey marly silts nor the tufaceous silts are present further to the east where earlier cores were taken, due to pronounced erosion at the base of the Lower Peat that seems likely to have taken place during the late Eemian.

Pollen spectra from the blue-grey marly-silts and the tufaceous silts are typical for the Eemian, while the molluscan fauna is exceptionally rich, with 71 terrestrial and 23 aquatic taxa (NEaar 12277-81; 13113-5; 13122-4; 13137-9; 13223-5; 13297-9; 13137; 13312-4; 15865-7) and many species typical of warm interglacial conditions. These include several biostratigraphical markers that have only ever been found in contexts linked with full interglacials in Central Europe and some that seem to have first appeared in Switzerland and adjoining areas during the Eemian, such as *Acicula lineata, Daudebardia brevipes* and *Daudebardia rufa*. This confirms the available stratigraphical, palynological and absolute dating evidence that these interglacial silts correspond to the Eemian.

2.2.3.2. Zell

Zell is located in central Switzerland, near the north-western edge of the Alps. Molluscs from Kiesgrube (gravel quarry) Meier, south of Zell were first studied by L. Forcart in the early 1940's (Erni *et al*., 1943), but most of this material seems to have been lost. The same location was resampled by A. Jayet during the mid-1940s, and more recently in a nearby profile by D. Kälin in 2019.

The Forcart and Jayet faunas were found in an 8 m sequence of tufaceous silty-sands, sands and sandy fine to medium gravels that seem to have been deposited by a river. These deposits were underlain by c.14 m of Hochterrasse fluvioglacial gravels, and overlain by another 20 m of fluvioglacial gravels that may date from MIS 4 (Preusser *et al*., 2001). D. Kälin returned to the site in 2019 and took new samples in c.7 m of silts, marly-silts and sandy-silts alternating with layers of fine to medium sandy gravel, and it is the shells from these new samples that have been analysed for this study (NEaar 14010-2; 14077-82). Palynological studies together with U/Th and OSL dating have shown that these deposits span from the start of the Eemian until the Early Würm (MIS 5e-MIS 5c; Küttel and Lotter, 1987; Wegmüller, 1996; Preusser *et al*., 2001; Frechen *et al*., 2007).

The molluscs from the Forcart and Jayet samples include a number of typical interglacial species, among which are several biostratigraphical markers that firmly place the faunas within the Eemian (Thew, 2024). These include *Acicula lineolata*, *Aegopinella nitidula*, *Aegopinella ressmanni*, *Discus perspectivus*, *Pagodulina pagodula* and *Ruthenica filograna*. The first two taxa have only ever been found at Zell, while the other four have also been found at Niederweningen (Thew, 2024). When compared to the sequence from Niederweningen, these faunas seem to correspond to a mid-phase of the Eemian, while those from the 2019 samples are fairly similar, but are missing four of the marker species mentioned above, indicating that they may represent an earlier phase of the Eemian.

2.2.3.3. Thalgut

Thalgut is located in west-central Switzerland near the north-western edge of the Alpine massif. The site is a gravel quarry that was first studied and sampled by C. Schlüchter in 1972 (Schlüchter, 1976). The molluscs analysed for IcPD come from a series of laminated lacustrine silts and sands exposed in the gravel quarry that also include macroremains from which pollen and OSL dating have since shown to be of Eemian age (Welten, 1988; Preusser and Schlüchter, 2004; Preusser *et al*., 2011, p.288). Among the molluscs are *Discus perspectivus*, which is typical of warm interglacials, and *Pagodulina pagodula*, which seems to be an indicator species for the Eemian in Switzerland (Thew, 2024). The lake silts are covered by thick gravel deposits from the last glacial period. In 1983, a core was sunk beneath the floor of the quarry that revealed earlier lacustrine deposits c.40 m below the Eemian lake sediments (Welten, 1988), but no samples have been analysed for molluscs from this earlier level.

Two sets of samples have been analysed for IcPD. The first (NEaar 12274-6) consisted of *Bithynia* opercula that had been either previously extracted from the lake silts or recovered by the sieving of 0.4 kg of unprocessed sample. Due to unexpectedly high IcPD values, a further 0.3 kg of the original 1972 sediment was sieved and a second series of opercula were extracted (NEaar 14071-3).

2.2.4. Holocene

To complete the series of IcPD samples from the Swiss Plateau, shell material was added from a series of Holocene sites: including one site where earlier deposits were already being investigated for this study (Sous-Terre 'upper level') together with other Holocene sites from across the Swiss Plateau (Boppelsen-Cholholz, Abri Unterkobel, Oberbipp, Hauterive-Champréveyres).

2.2.4.1. Sous-Terre 1

The *Bithynia* opercula analysed in this study (NEaar 12260-2) come from the lower part of a grey marly silty-sand with some fine-medium gravel (ST1, the upper level sampled for IcPD at this site; cf. section 2.2.2.2), which overlies an LGM basal till and is situated between 376.30 and 377.0 m asl, c.7 m above the present level of the Rhône (369.30 m asl; Jayet & Amberger, 1969). The molluscan assemblage is 85% aquatic, in keeping with this sediment representing an 8 m terrace deposit, contemporary with the 8-10 m terrace of Lake Geneva (cf. Schoeneich, 1998). The molluscs include the pioneer forest species *Discus ruderatus*, but none of the woodland taxa that appear during the late Preboreal. By contrast, the molluscs from the upper part of this terrace deposit (not sampled for IcPD) have eight more forest species, including five that are known to first appear during the late Preboreal. This evidence suggests that the analysed shells date from the earlier part of the Preboreal.

2.2.4.2. Boppelsen-Cholholz

This site is located in north-eastern Switzerland and was sampled by A. Jayet in 1948 from a Höhere Deckenschotter (HDS) outcrop at Wakern, near Boppelsen (Jayet, 1949). The shells were found in 3 m of brown tufaceous sandy-silt with frequent stones, charcoal fragments and mollusc shells (NEaar 14007-9), which lay beneath 1 m of Holocene colluvium. Beneath the sampled layer was over 6 m of sterile fluvioglacial gravels and sands that correspond to the HDS. The molluscs from this site were analysed because it had long been thought that they might be contemporary with the HDS terrace. The molluscan fauna appears to date from the early Boreal by comparison with well-dated Holocene sequences elsewhere in Switzerland (cf. Liniger and Thew, 2008, 2016, Thew 2022). The sediment in which these shells were found seems to represent the infilling of an erosional gully cut into the summit of the HDS gravels. This was c.3 m deep but only of limited extent, which might explain why later researchers were unable to locate this shell-bearing deposit.

2.2.4.3. Abri Unterkobel, Oberriet

Abri Unterkobel is located in north-eastern Switzerland, near the border with Austria. It is a rock-shelter in the Alpine Rhine Valley, with Mesolithic to Roman archaeological occupation levels (Wegmüller *et al*., 2013, Wegmüller 2022). The shells used for IcPD analysis (NEaar 12254-9) come from Middle Mesolithic layers dated by radiocarbon and molluscan biostratigraphy to the later Boreal, which have a molluscan assemblage dominated by forest and shade-loving species (Thew, 2022). These layers include occupation material and several hearths, while overlying levels dating from the Middle Neolithic include dung from stabled sheep/goats, some of which had been burnt.

2.2.4.4. Oberbipp

Oberbipp is located in the central part of western Switzerland. During the excavation of a Late Neolithic dolmen in 2011/12, mollusc shells were recovered from both the tufaceous sediments that lay beneath the dolmen and the infill of the burial chamber. The molluscan faunas from beneath the dolmen can be reliably attributed to the early to mid-Boreal, and is missing other woodland taxa that appeared between the late Boreal and the start of the Younger Atlantic, all of which were present in the Late Neolithic deposits within the dolmen. The worm granules and slug plates (NEaar 13300-2; 13341-3) come from the early/mid-Boreal layer, while the *Arianta*, *Fruticola* and *Cepaea* all come from the Late Neolithic/early Subboreal level (samples NEaar 13125-7; 13140-2; 13238-40).

2.2.4.5. Hauterive-Champréveyres, Lake Neuchâtel

The *Bithynia* operculae used in this study (NEaar 12251-3) come from a late 19th century beach deposit at Hauterive-Champréveyres at the north-western margin of Lake Neuchâtel, which was sampled in 1986 prior to motorway construction. This beach was formed when the level of Lake Neuchâtel was lowered suddenly by c.2.7 m during the late 1870's as a result of the *Premier Correction des Eaux du Jura*, causing severe erosion around the lake that led to the truncation of earlier lake sediments (Moulin, 1991).

2.3. Materials

Biominerals were analysed from 31 horizons from 18 sites. Six different types of biomineral were analysed: calcitic *Bithynia* opercula, slug plates and worm granules; and aragonitic *Arianta*, *Cepaea* and *Fruticola* shells (Table 1). The only material for which full closed system tests and an aminostratigraphic framework had previously been developed was the *Bithynia* opercula (Penkman *et al*., 2013; Tesakov *et al*., 2020). Small-scale pilot and unpublished IcPD studies had previously been undertaken on *Arianta* and *Cepaea* shell, slug plates and worm granules, but this represents the first widespread study on these fossil materials, as well as the first IcPD data on *Fruticola* shell.

Table 1: Samples analysed for the study. Morphostratigraphy where relevant: HDS: Höhere Deckenschotter, TDS: Tiefere Deckenschotter, HT: Hochterrasse, NT: Niederterrasse, HOL: Holocene. For qualitative assessment of evidence of age, from higher to lower probability: probably – likely – possibly. Materials are slug plates (SP), worm granules (WG), *Bithynia* opercula (B), *Fruticola* (F), *Arianta* (A) and *Cepaea* (C) shells.

Site and reference	**Geographical location** **Swiss Coordinates [°] (CH1903+/LV95)**	**Morph. str. unit**	**Evidence of age**	**Material/ Genus**
Irchel Plateau:		HDS	Early Pleistocene, controversy in age interpretations (A and B)	
Irchel Ebni: Ebni Silts	2687008/1267577		A) older than Hasli Formation based on lithostratigraphy (Graf, 1993) and clast petrography (Thew *et al.*, 2024), B) younger than Hasli Formation based on interpretation of cosmogenic data (Dieleman *et al.*, 2022a).	SP, WG
Irchel Hasli: Hasli Fm.	2688944/1265570		A) 2.2-1.8 Ma (small mammal remains, Bolliger *et al.*, 1996; Cuenca-Bescos, 2015; Thew *et al.*, 2024, molluscan assemblages, pollen, palaeomagnetic data); B) < 1.3 ± 0.1 Ma (isochron-burial dating, Dieleman *et al.*, 2022a)	SP, WG
Irchel Steig East/ Irchel Steig West: Hasli Fm.	2688548/1265629; 2688500/1265633		A) Same age as Hasli Fm. at Irchel Hasli (Graf, 1993), molluscan analysis, lithostratigraphy, B) younger than 0.9 ± 0.1 Ma (isochron-burial dating (Dieleman *et al.*, 2022a)	SP, WG, A, C
Irchel Amselboden	2687258/1266111		A) Same age as Hasli Fm. at Irchel Hasli (based on lithostratigraphy (Graf, 1993) and molluscan assemblages (Thew *et al.*, 2024)	F, C, SP, B

Irchel Hochwacht East: Hasli Fm.	2686077/1268269		A) Same age as Hasli Fm. at Irchel Hasli (based on lithostratigraphy (Graf, 1993), molluscs, pollen, paleomagnetic data (Thew *et al.*, 2024)	A, SP, C, B, WG
Irchel Hochwacht West: sandy lens above Hasli Fm.	2686045/1268256		Younger than Hasli Fm. (based on stratigraphic superposition) Hasli Fm. probably c.2.1-1.8 Ma (based on small mammals, molluscan assemblages and paleomagnetic data, Thew *et al.*, 2024),	
Albishorn-Bürglen		HDS	Early Pleistocene	
Albishorn-Bürglen 2: lenses in Albisboden-Schotter	2683325/ 1234575	Base HDS	Older than 1.8 Ma (based on molluscan assemblages (Thew, 2024)	B, SP, WG
Albishorn-Bürglen 1: silt and sands on top of Bürglen till	2683435/ 1234429	Upper HDS	Likely middle Early Pleistocene -possibly Eburonian probably younger than 1.8 Ma (based on mollusc assemblages (Thew, 2024) and pollen (pers. comm. M. Knipping)	B
Hungerbol: silts and fine sand		TDS	later Early Pleistocene	
Hungerbol 2	2708100/ 1282505		probably 1.8/1.7 – 1.1/1.0 Ma, possibly 1.2-1.0 Ma (based on molluscan assemblage, small mammal remains (only limited findings), pers. comm. O. Fejfar, and lithostratigraphic context (presence of glaciogenic sediments)	WG, SP, B, A, F
Hungerbol 1				WG, A,
Ecoteaux: lacustrine silts of layer 8	Loc A: 2556 360/1155 050 Loc B: 2555 370/1154 680	none	early Middle Pleistocene (Chibanian) Possibly MIS 15—(based on pollen, palaeomagnetic data and lithostratigraphic context (Pugin *et al.*, 1993)	B

Montfleury Core 1: sandy silts of 'Confignon Sequence' below 'alluvion-ancienne'	2494 400/1119 265	Rhône system	Middle Pleistocene (Chibanian) Likely MIS 11 (based on pollen and lithostratigraphic context (Lanterno *et al.*, 1981; Wegmüller *et al.*, 1995; Moscariello *et al.*, 1998), molluscs (Thew, 2024))	F
Sous-Terre 2: sandy silts below 'alluvion-ancienne'	2499 175/1117 750	Rhône system	Middle Pleistocene (Chibanian) Likely MIS 11 (based on pollen (Girard, 1970), molluscs (Thew, 2024) and lithostratigraphic context (Jayet and Amberger, 1969; Moscariello *et al.*, 1998)	F, A, C, SP, WG
Nuolen 1 and 3/Buechberg	est. 2710 160/1228 620 est. 2710 370/1228 440	HT	Middle Pleistocene (Chibanian) Probably MIS 7 (based on correlation to nearby profiles with pollen analysis (Welten, 1988, Schindler (2004, p.13-31)) and molluscan analysis (Thew, 2024))	B, A, C, WG
Grandson	2539 300/1184 700	HT	Middle Pleistocene (Chibanian) Probably MIS 7 (based on pollen analysis (Welten, 1988) and lithostratigraphic correlations (Jordi, 1996, 2006)	B, A
Petit Sacconex 1994	2498 930/1119 760	Rhône system	Middle Pleistocene (Chibanian) Possibly early MIS 6 or somewhat older (based on lithostratigraphy; Jayet *et al.*, 1961)	A, WG
WHO	2499 230/1120 850	Rhône system	Middle Pleistocene (Chibanian) Possibly early MIS 6 or somewhat older (based on lithostratigraphy; pollen evidence in Reynaud, 1982, fig.11)	A, SP

Zell 2019	2636 552/1220 110-11	HT	Late Pleistocene MIS 5e (based on molluscan analysis, this study, and lithostratigraphic correlation to adjacent profiles with pollen analysis and U/Th and OSL dating (Küttel and Lotter, 1987; Wegmüller, 1996; Preusser *et al*., 2001; Frechen *et al*., 2007)	A, WG, SP
Thalgut	2608 990/1186 615	HT	Late Pleistocene MIS 5e (based on pollen analysis and luminescence dating (Welten, 1988; Preusser and Schlüchter, 2004) as well as molluscan analysis, Thew, 2024)	B
Niederweningen	15A: A: 2670 369/1262 15B: 2670 409/1262 380 18/2: 2670 514/1262 322 18/3: 2670 428/1262 363	none	Late Pleistocene MIS 5e (based on pollen analysis, molluscan analysis (Miocic *et al*., forthcoming), and lithostratigraphic correlation to adjacent profiles (Welten, 1988; Anselmetti *et al*., 2010; Dehnert *et al*., 2012) with pollen analysis and luminescence dating	B, A, F, C, SP, WG
Sous-Terre 1	2499 175/1117 750		Holocene 10 m terrace of the Rhône Preboreal (based on molluscan assemblages, this study)	B
Boppelsen-Cholholz	Nagra: 2673656/ 1258899 Jayet: 2673 800/1258 850		Holocene sediments overlying HDS deposits (sampled by NAGRA, but sterile for biological material) Boreal (based on molluscan assemblages, Thew 2024)	A
Abri Unterkobel, Oberriet	2759 659/2242 699		Holocene Boreal	A, F

			Boreal (Middle Mesolithic layer dated with archaeological material, radiocarbon and molluscan analysis; Thew 2022)	
Oberbipp	2616 765/1234 395		Holocene Boreal and Subboreal (based on molluscan assemblages (Thew, 2024) and archaeological dating)	F, A, C, SP, WG
Hauterive-Champréveyres	2564 480/1206 390		Holocene Late 19th beach deposit (historical record, after the “Premier Correction des Eaux du Jura;” Moulin 1991)	B

2.4. Analysis

All samples were prepared using the procedures of Penkman *et al*. (2008) to isolate an intra-crystalline protein by oxidation, with an individual biomineral forming each sample. In brief, two subsamples were taken from each single biomineral: one fraction was directly demineralised and the free amino acids analysed (referred to as the 'free' amino acids, FAA), and the second was hydrolysed at 110°C for 24 hours to release the peptide-bound amino acids, thus yielding the ‘total hydrolysable amino acid fraction (THAA). Samples were analysed in duplicate by RP-HPLC using a modified method of Kaufman and Manley (1998), with standards and blanks run alongside samples. During hydrolysis, both asparagine and glutamine undergo rapid irreversible deamination to aspartic acid and glutamic acid, respectively (Hill, 1965). It is therefore not possible to distinguish between the acidic amino acids and their derivatives and they are reported together as Asx and Glx, respectively.

The D/L values of aspartic acid/asparagine, glutamic acid/glutamine, serine, alanine and valine (D/L Asx, Glx, Ser, Ala, Val) and the concentrations of Ser and Ala ([Ser]/[Ala]) were then assessed to provide an overall estimate of intra-crystalline protein decomposition (IcPD). These amino acids are the best chromatographically resolved enantiomer pairs for calcium carbonate shells in general (Powell *et al*., 2013), and between them also cover a wide temporal range (Penkman *et al*., 2011). The D/L of an amino acid will increase with increasing time, whilst the [Ser]/[Ala] value will decrease. Each amino acid racemises at different rates, and therefore is useful over different timescales. The D/L of Ser is less useful for geochronology; the relatively fast breakdown of free Ser (which tends to be more racemised) means there is a loss of free serine as samples increase in age, resulting in a single D/L value representing more than one time-point in samples of this age (Penkman *et al*., 2008). However, D/L Ser is reported here as aberrant values are useful indications of contamination (e.g. Williams and Smith, 1977; Kosnik and Kaufman, 2008). The IcPD of the FAA and THAA subsamples can also be used to recognise any compromised samples, as in a closed system, the FAA and THAA D/Ls should be highly correlated (e.g., Preece and Penkman, 2005).

3. Results and Discussion

Samples have been colour-coded according to independent evidence of age from each site (Table 1: green = Holocene & Late Glacial (Niederterrase); blue = Late –Mid Pleistocene (Hochterrasse); olive green = late Early Pleistocene - Tiefere (Lower) Deckenschotter; red/orange = older Early Pleistocene - Höhere (Higher) Deckenschotter.

Some pilot work had been undertaken on isolation of the intra-crystalline fraction of the non-opercula biominerals (the aragonitic shells of *Fruticola fruticum, Arianta arbustorum*, *Cepaea hortensis* and the calcitic slug plates and worm granules), but this represents the first comprehensive study of the intra-crystalline fraction in fossil specimens of these biominerals. After bleaching, an intra-crystalline fraction of amino acids was retained in each biomineral tested. Whether this intra-crystalline fraction comprises a closed system can be tested through high-temperature experiments (Penkman *et al*., 2008; Demarchi *et al*., 2011), but in the absence of these, we explore the general IcPD behaviour and its potential for geochronology in these biominerals.

3.1. *Bithynia* opercula

Bithynia opercula are mineralised in the form of calcite, and this mineralogically stable form of calcium carbonate has been shown to provide a closed system repository for the intra-crystalline amino acids in opercula as old as the Eocene (Penkman *et al*., 2013).

Most of the opercula show closed system behaviour with good correlation between the FAA and THAA fractions (Fig. 1). The small opercula fragments from Irchel Amselboden and Albishorn Bürglen have very low sample concentrations, too low indeed for accurate D/L determination, which combined with their compositions (Fig. 2) are consistent with their being of significant age. Irchel Hochwacht 13+12 are consistent in Ala and Val, but their high level of degradation compromises their Asx and Glx D/L data.

Asx is one of the fastest racemizing of the amino acids discussed here (as it can racemize whilst still peptide bound), enabling good levels of resolution for younger age sites, but decreased resolution in Early and Middle Pleistocene material. There were very low concentrations of Asx (a relatively unstable amino acid) in the Irchel Hochwacht, Hungerbol 2 and Amselboden 21 samples, so the D/L Asx is not accurately determinable. For samples where D/L Asx was determined, Ecoteaux showed the highest levels of racemisation, followed by Thalgut. Nuolen, Grandson and Niederweningen showed similar levels of breakdown, but lower than Thalgut. The Sous-Terre upper level showed even lower Asx D/Ls. The data from Hauterive-Champréveyres was variable between samples, possibly because the material is a mix of redeposited Holocene opercula and modern examples, but showed the lowest levels of racemisation, indicating that it is the youngest site of the set.

Glx is one of the slower racemizing amino acids discussed here and so the level of resolution from young sites is less than that seen with faster racemizing amino acids such as Asx. Glx has an unusual pattern of racemization in the free form, due to the formation of a lactam (see Walton, 1998). As this lactam cannot be derivatised and so is unavailable for analysis, this results in relatively low precision for the FAA D/L, particularly in younger samples. For D/L Glx, where concentrations are high enough for accurate measurement, the highest levels of racemisation are observed in Hungerbol 2, with significantly lower levels in Ecoteaux, and then significantly lower again for Thalgut (Fig. 1), indicating a large difference in age between these three sites. Nuolen, Niederweningen and Grandson show even lower but similar Glx D/Ls to each other, with very little Glx racemisation in Sous-Terre 1 and Hauterive-Champréveyres (Fig. 1). This data is consistent with the Asx D/L pattern, but unlike Asx D/L, Glx is able to discriminate better between the older samples due to the slower rate of racemisation for this amino acid.

Alanine (Ala) is a hydrophobic amino acid, whose concentration is partly contributed from the decomposition of other amino acids (notably serine). Ala racemises at an intermediate rate, so it is helpful in distinguishing ages at a range of timescales. Irchel Hochwacht and Hungerbol 2 show the highest levels of racemisation (Fig. 1), with Ecoteaux slightly lower, and Thalgut significantly lower. Nuolen, Grandson and Niederweningen again show lower D/Ls, similar to each other. Sous-Terre 1 and Hauterive-Champréveyres again show the lowest levels of breakdown, consistent with their Holocene age.

Valine (Val) has extremely low rates of racemisation, and as the concentration of Val is quite low, the difficulty of measuring the D/L accurately leads to higher variability. It does, however, still prove useful for age discrimination, particularly for older material. The Val D/L in the FAA and the THAA fractions support the other amino acids, with Irchel Hochwacht and Hungerbol 2 showing the highest levels of breakdown and likely to be of significant age, certainly Early Pleistocene. Ecoteaux is significantly younger, in line with pollen data that suggests the deposits probably date from the early Middle Pleistocene (see Section 2.2.2.1). Thalgut is younger still; interestingly the two sets of Thalgut samples, which show very similar data in the other amino acids, show some differentiation in Val. This is unexpected; we do not know the history of these samples, and so it is possible that storage conditions or drying of the samples before processing may have occurred. We recommend this data should be treated with caution, and that new sediments are recovered from the site for analysis. Nuolen, Grandson and Niederweningen show low Val D/Ls, with Sous-Terre 1 and Hauterive-Champréveyres showing almost no breakdown in Val.

In summary, the opercula samples from these sites show closed system behaviour and can therefore be used for age estimation. Assuming the same effective diagenetic temperatures experienced at all the sites, and given the temporal level of resolution possible using this biomineral, the relative age order predicted by the *Bithynia* opercula is therefore (oldest to youngest):Irchel Amselboden & Albishorn Burglen ≫ Irchel Hochwacht 19 ≥ Hungerbol 2 ≫ Ecoteaux ≫ Thalgut > Nuolen ≈ Grandson ≈ Niederweningen > Sous-Terre 1 > Hauterive-Champréveyres. The material from the Höhere Deckenschotter shows very high levels of degradation, greater than that observed in early Early Pleistocene opercula from northern Europe (Penkman *et al*., 2013) and the East European Plain (Tesakov *et al*., 2020). While studies into calibrating the aminostratigraphies between different regions are ongoing, this supports an early Early Pleistocene age for the Höhere Deckenschotter sites analysed here.

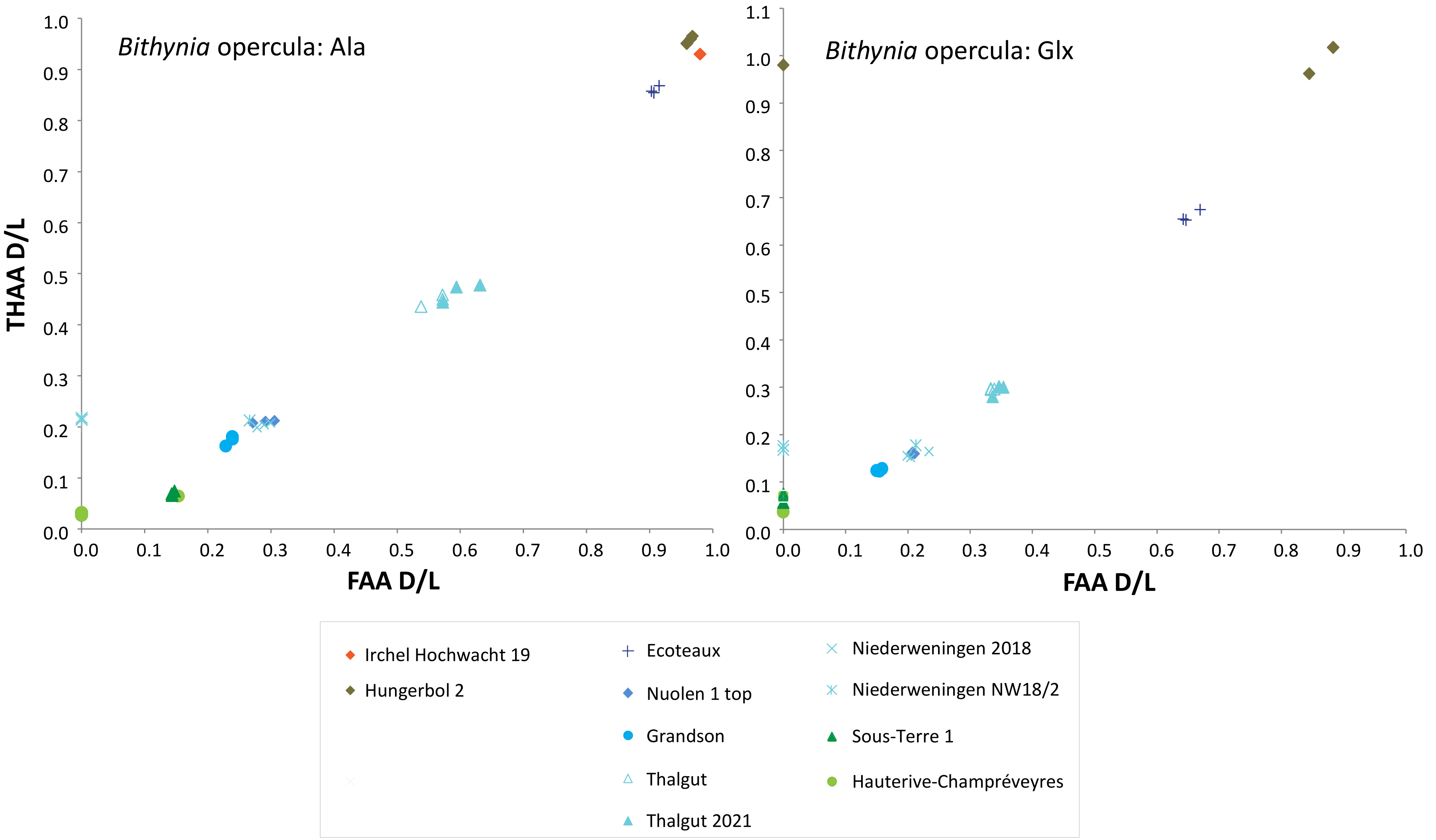

Figure 1: Means of the analytical replicates for THAA D/L vs FAA D/L for Ala and Glx in *Bithynia* opercula from Switzerland. Colour-coding is based on the morphostratigraphy: green = Holocene & Late Glacial (Niederterrase); blue = Late –Mid Pleistocene (Hochterrasse); olive green = late Early Pleistocene - Tiefere (Lower) Deckenschotter;

red/orange = older Early Pleistocene - Höhere (Higher) Deckenschotter. N.B. Zero values along the x or y-axes are due to the concentrations being too low to measure D/L accurately; for Hungerbol 2 this is because the amino acids are very degraded; for the younger sites at Sous-Terre 1 and Hauterive-Champréveyres, this is because so little peptide bond hydrolysis has occurred that there are very few free amino acids; for Niederweningen NW18/2, two of the opercula were too small to enable a FAA analysis. Data from Albishorn Bürglen and Irchel Amselboden are not plotted in these D/L figures as the levels of protein degradation in these samples were too high, consistent with their stratigraphic position as being the oldest in the sample set**.**

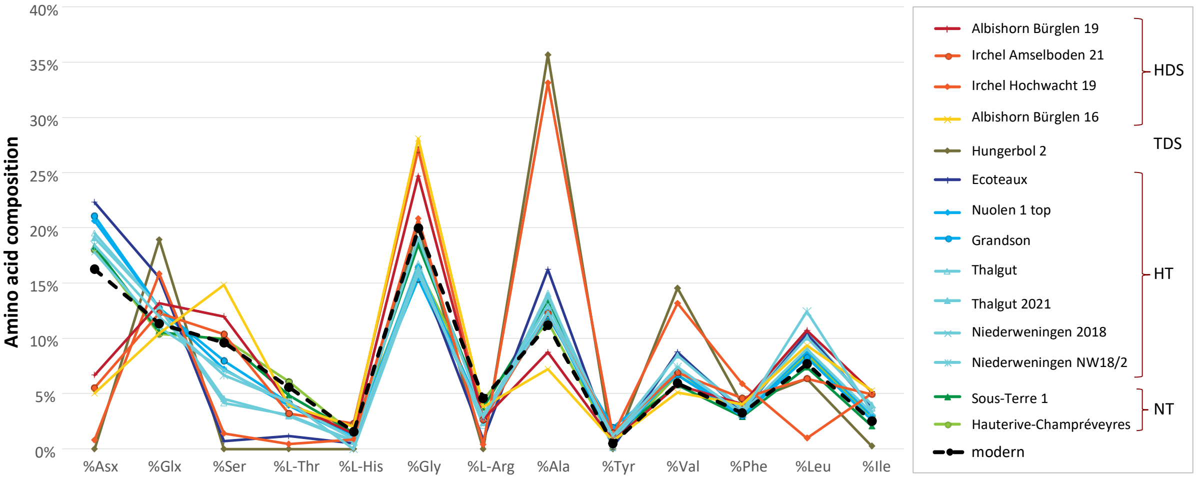

Figure 2: Means of the analytical replicates for THAA % composition in *Bithynia* opercula from Switzerland, compared to modern material. The high levels of degradation in the HDS and TDS samples (e.g. low %Asx, higher %Glx) is consistent with significant age.

For most of the sites, this aminostratigraphy supports the stratigraphic interpretation. It is no surprise, for example, to find that both recent (late 19th/20th century) *Bithynia* opercula and older (possibly Older Atlantic) redeposited opercula were present within the Hauterive-Champréveyres sample, because the major fall (2.7 m) in lake-levels in the 1870s led to significant erosion and the mixing of earlier material within the subsequent lake beach deposit. Two sites warrant further comment: Thalgut and Niederweningen.

Thalgut was expected to be Late Pleistocene in age because of OSL dating and pollen evidence (see Section 2.2.3.3), so the high IcPD in the opercula from this site is unexpected. This cannot be due to sampling problems, because when Schlüchter studied the site in the early 1970s the only interglacial lake sediments exposed were those that have subsequently been dated to the Eemian (Welten, 1988; Preusser and Schlüchter 2004). Issues concerning heating during laboratory processing were therefore suspected, but additional analyses from material sieved from the same sediments also show high levels of IcPD (NEaar 14071-3), confirming that these high IcPD values are repeatable. It is possible that historic heating of bulk sediments for drying may be responsible for these anomalous values, and therefore potentially needs to be considered for other archive samples.

Niederweningen seems to correspond to the Eemian (Section 2.2.3.1), so was expected to show lower levels of IcPD than Grandson and Nuolen, which have been correlated with MIS 7 via pollen and stratigraphic relationships (Sections 2.2.2). More detailed interpretation may be resolvable by increasing the number of opercula analysed from this site.

3.2. *Fruticola* shells

Over geological timescales aragonitic shells such as Fruticola can be more susceptible to mineral diagenesis than the more stable calcite of materials such as slug plates (Land, 1967; Penkman *et al.*, 2010, 2013). It is therefore important to identify this where it has occurred, as any mineral diagenesis may compromise the age signal (Preece and Penkman, 2005). In general, a good correlation between the FAA and THAA D/Ls is observed (Fig. 3), which indicates closed-system behaviour. However, one of the Montfleury samples (12264, identified in red outline) shows divergence from the expected pattern in the THAA fraction, and therefore data from this shell should be rejected due to non-closed system behaviour.

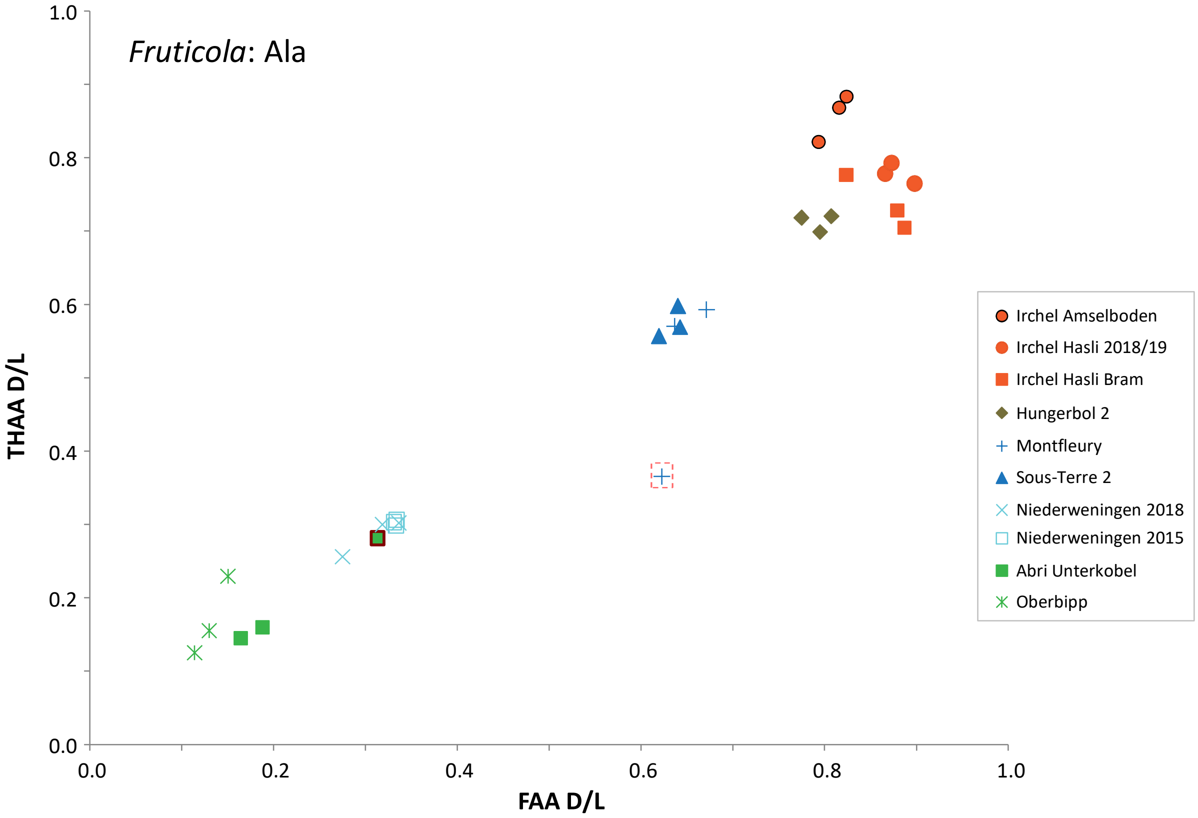

Figure 3: THAA D/L vs FAA D/L Ala in *Fruticola* shells from Switzerland. One sample from Montfleury (outlined in red) showed divergence from closed-system behaviour; one sample from Abri Unterkobel (dark brown border) shows much higher D/Ls than the other two samples, potentially due to hearth heating.

The Irchel samples show the highest levels of racemisation of all the sites (Fig. 3); given the limited number of samples analysed here, it is not possible to further temporally discriminate these Irchel samples based on *Fruticol*a data alone. Hungerbol 2 shows slightly lower IcPD values, consistent with an age during a later part of the Early Pleistocene. Montfleury and Sous-Terre 2 exhibit intermediate D/L values, similar to each other, and consistent with a Middle Pleistocene age. Next lowest are Niederweningen 2018 and 2015, which have similar levels of IcPD to each other, consistent with the stratigraphic age attribution. Samples from Abri Unterkobel and Oberbipp show the lowest levels of breakdown, consistent with their Holocene age. However, there is a surprisingly high level of IcPD in one of the samples from Abri Unterkobel (12259) compared with the two others (Fig. 3). This is likely to have been caused by anthropogenic heating of this shell; although none of the analysed shells from this rock-shelter site show any visible signs of burning, localised *in situ* heating of the layers occurred due to the use of hearths at regular intervals and the burning of dung accumulations during Neolithic times when the abri (shelter) was used to stable sheep and goats (Wegmüller 2022).

This first IcPD data from *Fruticola* shell indicates that for most samples this biomineral does retain closed system behaviour as far back as the Early Pleistocene. Assuming the same effective diagenetic temperatures experienced at all the sites, and given the temporal level of resolution possible using this biomineral, the relative age order predicted by the *Fruticola* shell is therefore (oldest to youngest): Irchel Amselboden 21 ≈ Irchel Hasli 2018/19 ≈ Irchel Hasli Bräm > Hungerbol 2 ≫ Montfleury ≈ Sous-Terre 2-≫ Niederweningen 2018 ≈ Niederweningen 2015 > Abri Unterkobel > Oberbipp. This fits well with the hypothesised order of sites based on independent evidence of age; further analyses would clarify the level of natural variability within this biomineral.

3.3. *Arianta* shells

A correlation between the FAA and THAA D/Ls is observed (Fig. 4), which indicates potential closed-system behaviour. However, the Hungerbol 2 sample (12247; SwHAa, identified in red outline) shows divergence from the expected pattern in the THAA fraction, and therefore data from this shell should be rejected. This divergence from closed system behaviour is consistent with the surface alteration due to post-depositional weathering visible on some of the *Arianta* shells from Hungerbol 2. Two of the three Niederweningen 2018 samples also show IcPD patterns consistent with non-closed system behaviour (outlined in red). One sample from Irchel Steig also indicates non-closed system behaviour. As with all aragonitic shells, this is likely due to diagenetic transformation of some of the fossil mineral from aragonite to calcite.

The data from Abri Unterkobel is consistent within an individual sample, but variable between samples, similar to that observed in the *Fruticola* material from this site. As there is little evidence of vertical movement or reworking of material within the rock-shelter sediments, it seems likely that differential heating has led to acceleration of the protein breakdown in two of the three shell samples. It is therefore unsurprising that the shell samples from this site show differential levels of degradation, so it is only the youngest ratios that are likely to be indicative of age.

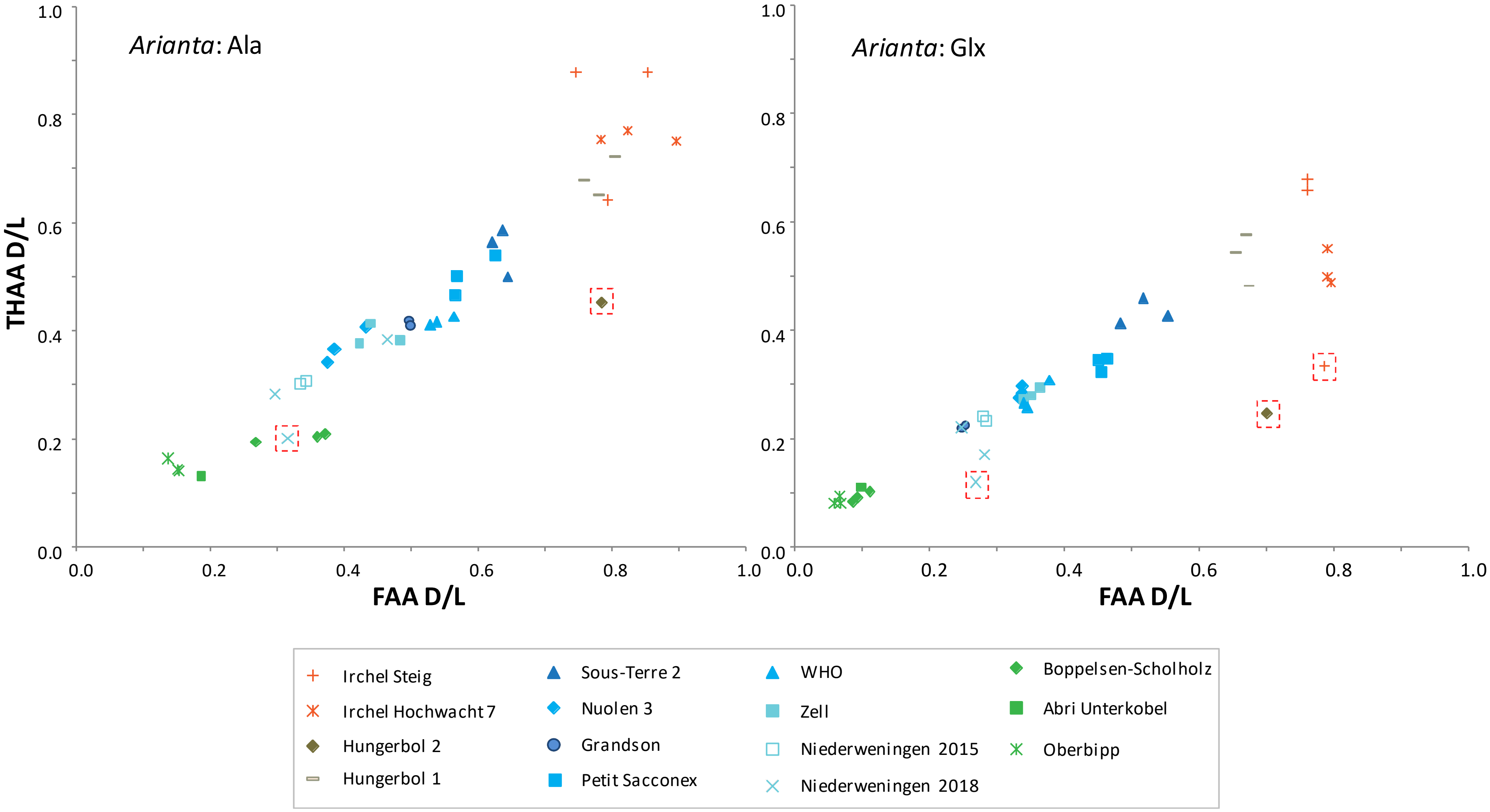

Figure 4: THAA D/L vs FAA D/L for Ala & Glx in *Arianta* shells from Switzerland. One sample from Hungerbol 2 and two samples from Niederweningen 2018 (outlined in red) showed divergence from closed-system behaviour. Only the unheated shells from Abri Unterkobel are shown.

The shells from Irchel Steig and Irchel Hochwacht show the highest levels of protein breakdown of the non-compromised material (Fig. 4), with Hungerbol 1 samples showing somewhat less degradation. Sous-Terre 2 shows intermediate values, but higher than Petit Saconnex and WHO. Zell, Nuolen 3 and Grandson are similar to each other. As two of the Niederweningen 2018 samples show non-closed system behaviour, the age interpretation is based on the single non-compromised sample, which shows lower IcPD than the Middle Pleistocene sites and similar to Niederweningen 2015. Boppelsen-Cholholz, the potentially unheated sample from Abri Unterkobel, and Oberbipp show the lowest levels of IcPD, consistent with their Holocene age.

In summary, this first IcPD data from fossil *Arianta* shell indicates that for most samples, this biomineral does retain closed system behaviour as far back as the Early Pleistocene. However mineral diagenesis of the aragonitic shells compromises their IcPD signal, and so it is important to select only un-weathered shells for analysis. Assuming the same effective diagenetic temperatures experienced at all the sites, the relative age order predicted by the *Arianta* shell is therefore (oldest to youngest): Irchel Steig ≈ Irchel Hochwacht 7 > Hungerbol 1 > Sous-Terre 2> Petit Saconnex > WHO > Zell ≈ Nuolen 3 ≈ Grandson > Niederweningen 2015 ≈ Niederweningen 2018 > Boppelsen-Cholholz (Ala) > Abri Unterkobel ≈ Oberbipp.

This sequence for the most part corresponds to what could be predicted from existing stratigraphic and dating evidence, with the exception of the 2019 samples from Zell, which should equate to the earlier part of the Eemian (see Section 2.2.3.2) and therefore would have been expected to have IcPD values similar to those of Niederweningen. As there was no heating during sample preparation and there is little chance of confusion during sampling, given that the fossiliferous deposits are sandwiched between two thick units of fluvioglacial gravel, the reasons for such a discrepancy remain unclear. The values from Petit Saconnex and WHO should be rather similar as they seem to come from the same stratigraphic unit, although the shells from WHO are slightly more weathered than those of Petit Saconnex. The values from both sites were expected to be younger than both Nuolen and Grandson on stratigraphic grounds; this is not confirmed by the amino acid geochronology, but may be due to a lack of temporal resolution in this taxon.

3.4. *Cepaea* shells

In general, a correlation between the FAA and THAA D/Ls is observed (Fig. 5), which indicates potential closed-system behaviour for this biomineral. However, there is quite a high degree of variability between samples from the same site, especially with older samples, and in Val. *Cepaea* is an aragonitic shell, so mineral diagenesis is likely. Due to the limited dataset for this biomineral, the closed system trendline is not currently clear, so only one sample (from Irchel Steig) has been marked as compromised. However, one sample from Sous-Terre 2, as well as samples from Irchel Hochwacht, Irchel Hasli 1994/95 and Irchel Steig plot in a region below the likely trendline, so data from these samples should be treated with caution.

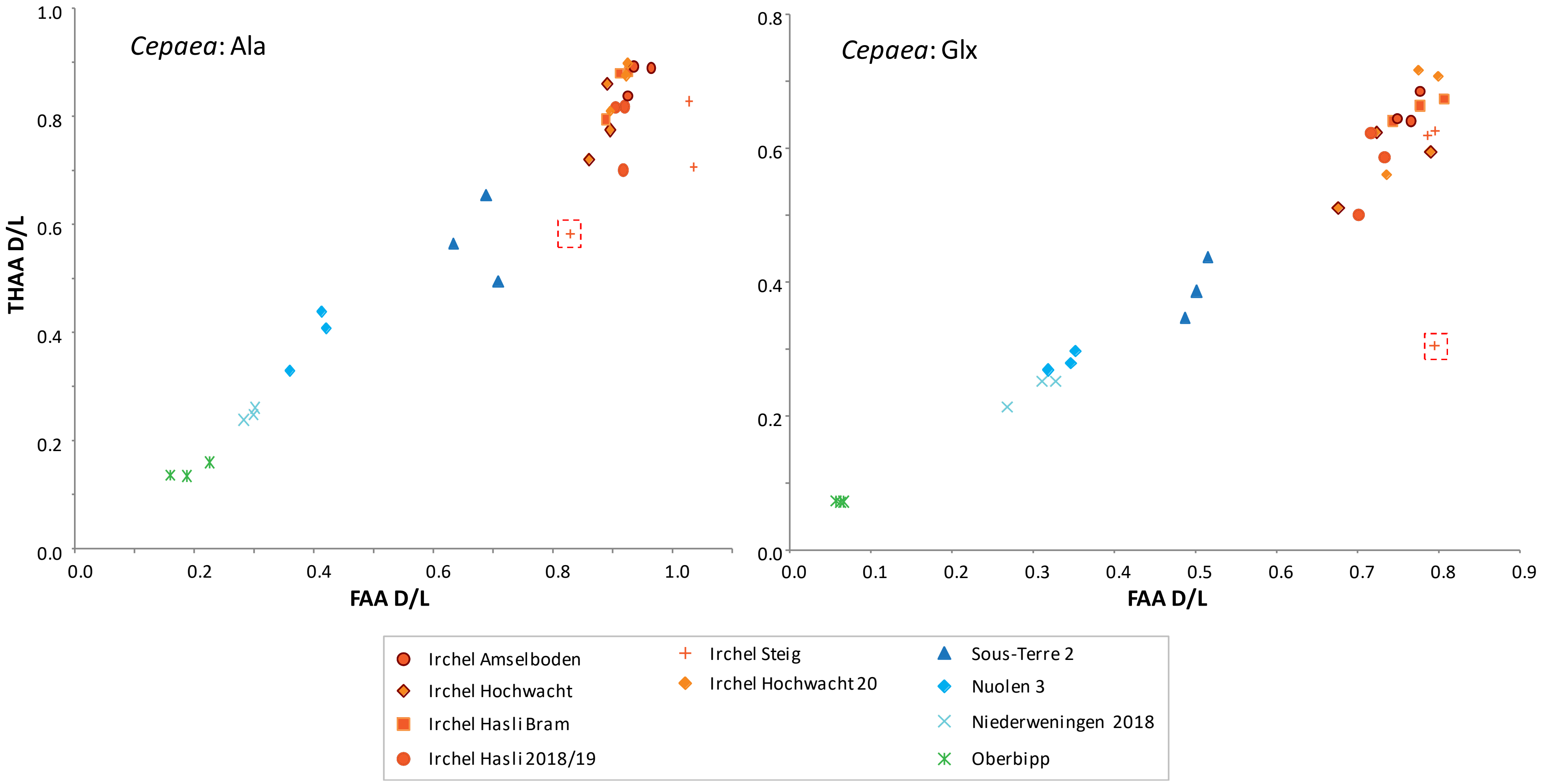

Figure 5: THAA D/L vs FAA D/L for Ala & Glx in *Cepaea* shells from Switzerland. One sample from Irchel Steig (outlined in red) showed potential divergence from closed-system behaviour

The shells from the Irchel Plateau show the highest levels of protein breakdown in *Cepaea* (Fig. 5). The samples from Irchel Hochwacht and Irchel Hasli 1994/95 also show very high levels of IcPD, but potential indications of non-closed system behaviour. If these Irchel Hasli samples have undergone some mineral diagenesis, then the higher IcPD values are likely to be the most useful indicator of age. Despite significant variability within this group of sites, the high levels of IcPD are consistent with an Early Pleistocene age. Sous-Terre 2 shows intermediate values, with one sample potentially falling off a closed-system trendline. Nuolen 3 shows less IcPD than Sous-Terre 2, and slightly more degradation than Niederweningen 2018. Oberbipp has the lowest levels of IcPD, consistent with its Holocene age.

In summary, this first IcPD data from fossil *Cepaea hortensis* shell indicates that for many samples, this biomineral does retain closed system behaviour as far back as the Early Pleistocene, but mineral diagenesis of these aragonitic shells may be exhibited. Assuming the same effective diagenetic temperatures experienced at all the sites, and given the temporal resolution of this biomineral, the relative age order predicted by the *Cepaea* shell is therefore (oldest to youngest): Irchel Amselboden ≈ Irchel Hochwacht ≈ Irchel Hasli Bräm ≈ Irchel Hasli 1994/95 ≈ Irchel Steig ≈ Irchel Hochwacht L20 ≫ Sous-Terre 2≫ Nuolen 3 lower > Niederweningen 2018 ≫ Oberbipp.

Stratigraphically, the shells from Irchel Amselboden and Irchel Hochwacht should be slightly older than those from Irchel Hasli Bräm, Irchel Hasli 1994/95 and Irchel Steig, whilst those from Irchel Hochwacht L20 should be somewhat younger, but this cannot be seen in the IcPD data, due to reduced temporal resolution at these high levels of IcPD. Interestingly, unlike the *Bithynia* opercula, the values for *Cepaea* from Niederweningen are less degraded than those of Nuolen.

3.5. Slug plates

The internal shells of slugs (slug plates) are mineralised in the form of calcite, and may therefore provide a diagenetically stable biomineral for amino acid analysis. Unfortunately, it is frequently impossible to identify slug plates to genus level, which is likely to influence the rate of the IcPD reactions and therefore the variability of the D/L values. Some pilot work has been undertaken on isolation of the intra-crystalline fraction of slug plates (Pope, 2010), but this represents the first wider study of the intra-crystalline fraction of fossil specimens of this biomineral. In general, a correlation between the FAA and THAA D/Ls is observed (Fig. 6), which indicates potential closed-system behaviour for this biomineral, except for the Hungerbol samples. However, there is quite a high degree of variability between samples from the same site, especially with older samples.

The shells from Irchel Ebni show the highest levels of protein breakdown in the slug plates (Fig. 6), which is consistent with the stratigraphy. The other Irchel samples also show high levels of IcPD, but interestingly the extent of racemisation in the slow-racemising amino acids is not as high as that seen from the same sites for other biominerals. This hints that the rates of the reactions in slug plates may be slower, which would result in a loss of temporal resolution, but increase the temporal range for this biomineral. The Sous-Terre 2 samples are intermediate in IcPD, with WHO showing less IcPD and then Zell and Niederweningen 2018. The Oberbipp samples are again the lowest of the suite, consistent with their Holocene age.

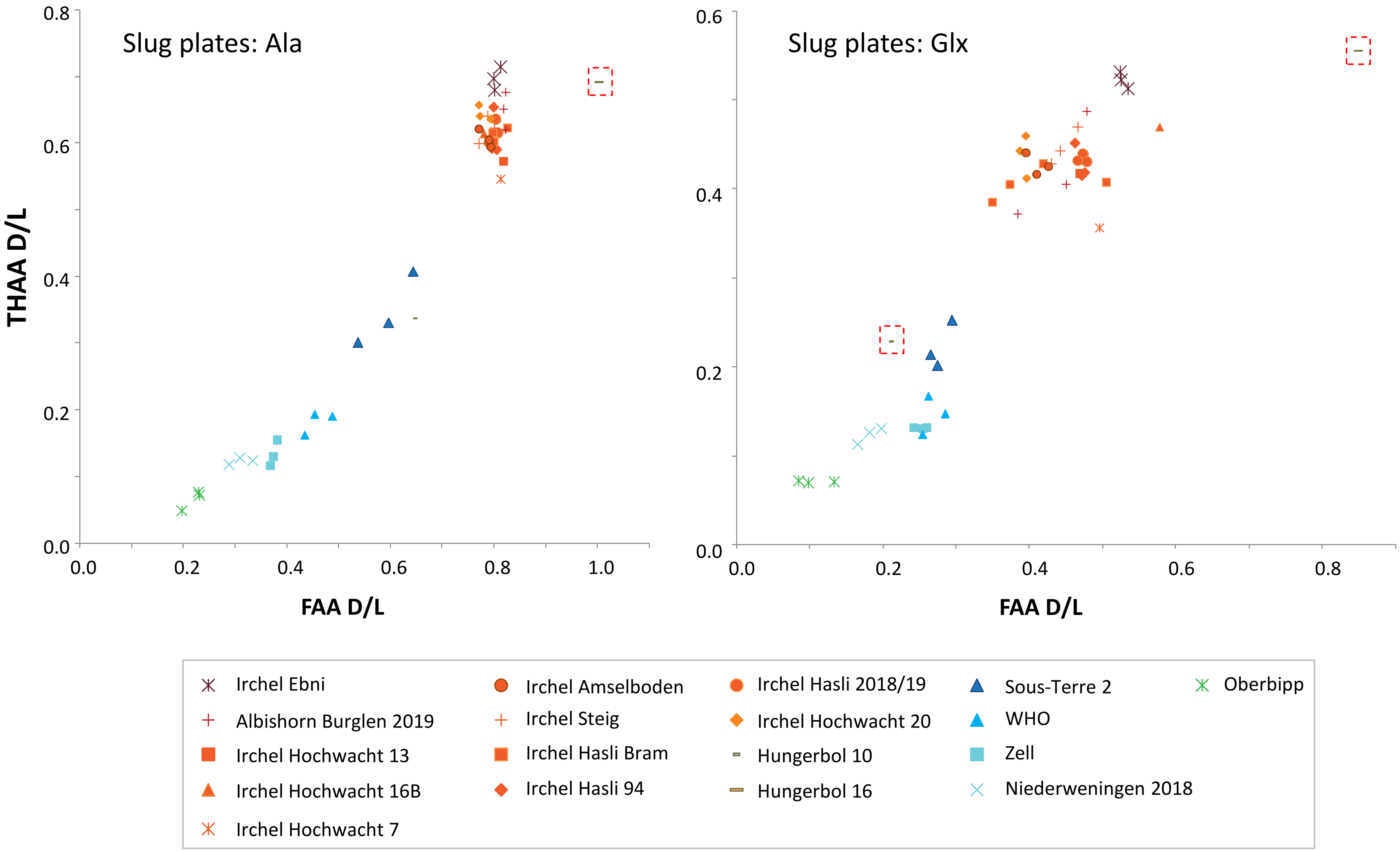

Figure 6: THAA D/L vs FAA D/L for Ala & Glx in slug plates from Switzerland. Both single samples from Hungerbol (outlined in red) show potential divergence from closed-system behaviour; more samples need to be analysed from this site before age estimation is attempted

In summary, this first IcPD data from fossil slug plates indicates that for most samples this biomineral does retain closed system behaviour as far back as the Early Pleistocene. The relatively high variability in some sites may be due to more than one genera being analysed. Assuming the same effective diagenetic temperatures experienced at all the sites, the relative age order predicted by the slug plates is therefore (oldest to youngest): Irchel Ebni > Irchel Hochwacht ≈ Irchel Amselboden ≈ Irchel Stieg ≈ Irchel Hasli Bräm ≈ Irchel Hasli 1994/95 ≈ Irchel Hasli 2018/19 ≫ Sous-Terre 2> WHO ≈ Zell > Niederweningen 2018 ≫ Oberbipp.

Stratigraphically, the slug plates from Irchel Amselboden and Irchel Hochwacht should be slightly older than those from Irchel Hasli Bräm, Irchel Hasli 1994/95, Irchel Hasli 2018/19 and Irchel Steig, while those from Irchel Hochwacht L20 should be somewhat younger, but this cannot be seen in the IcPD data, which is likely due to a lack of temporal resolution in samples of this age. Zell does seem to be younger than WHO, as the latter site is thought to be early MIS 6 or even older, while Zell is early Eemian, although it has IcPD slightly greater than those from Niederweningen. This was also observed in *Arianta*, suggesting that this may be linked with all material from Zell.

3.6. Worm granules

Certain genera of earthworms, including *Lumbricus, Aporrectodea*, *Octolasion* and *Allolobophora* produce granules of calcium carbonate in calciferous glands and excrete them into the sediment, with *Lumbricus* being the most prolific in the production of these granules (Canti, 1998). These granules contain a high proportion of calcite (Canti, 1998; Canti and Piearce, 2003; Hodson *et al*., 2015) and may therefore provide a diagenetically stable biomineral for amino acid analysis. It has been proposed that proteins, along with other organic components, are incorporated into the granules during the initial precipitation of calcium carbonate as amorphous calcium carbonate (ACC) spherulites in the calciferous glands (Briones *et al*., 2018; Mandera *et al*., 2023). Organics stabilise the ACC as a milky fluid, which is then transported to the worm's oesophageal pouches where it coalesces and crystallises to form the granules (Robertson, 1936; Morgan, 1981; Gago-Duport *et al*., 2008).

As an excretion product (rather than the skeletal biominerals analysed for the other taxa), it should be noted that the protein control and mineral stabilities may be more varied. There is no control of the structure of the granule, or the organics incorporated, by the calciferous gland. Furthermore, the chemical composition of the soil in which the worm lives influences the quantity of organic material incorporated into the crystal (Mandera *et al*., 2023). As such the composition of protein and stability of the mineral is likely to be more varied when compared to that of skeletal biominerals. It is also currently impossible to unequivocally identify fossil worm granules to species level, which may impact on the variability of the IcPD data. The *Arion* slug genus is also known to produce calcareous granules within their mantle, which are preserved in the soil following the slug's death (Canti, 1998). However these don't have the same morphology, and so we were careful to only sample typical worm granules.

Despite these possibly confounding factors, in general there is a correlation between the FAA and THAA D/Ls (Fig. 7), which indicates potential closed-system behaviour for this biomineral. However, there is a very high level of variability between samples from the same site. As this is the first detailed dataset that has been collected on worm granules, it is not possible to define precisely where the closed-system trendline is likely to plot, so as yet no samples have been identified as definitely non-closed system. However, several samples fall further away from the likely trendline for closed system behaviour, given the patterns expected based on other biomineral behaviour. These include three samples from Irchel Ebni, two samples from Irchel Hasli 2018/19, and one sample from Oberbipp. In addition, all the samples from the Early Pleistocene site of Irchel Hasli 1994/95 showed very low levels of IcPD, with low D/L values, high concentrations of amino acids and low levels of peptide bond hydrolysis. Given that earthworms are active within sediments, there is greater potential for the intrusion of younger material when analysing this biomineral. This is very likely to have been the case for the Irchel Hasli 1994/95 samples, as modern worm action was observed during excavation.

Given the high variability within sites, as well as the relatively large number of samples that are likely not to show closed system behaviour, the data from the worm granules should be interpreted with caution. However, certain age indications are still present in the worm granule dataset.

The oldest of the worm granules are the Irchel sites, along with Albishorn Bürglen, consistent with their Early Pleistocene age, the exception being the granules from Irchel Hasli 94/95 which clearly represent intrusive modern elements. The Hungerbol material shows slightly lower levels of IcPD, supporting the *Fruticola* dataset, so may date from somewhat later during the Early Pleistocene. Sous-Terre 2 shows intermediate levels of IcPD, consistent with its Middle Pleistocene age, while the Petit Saconnex, Zell and Niederweningen 2018 samples show lower levels of IcPD, supporting the data from the other biominerals. Nuolen's samples are slightly lower than expected from IcPD in the other biominerals; there may have been intrusion of younger worm granules into the Middle Pleistocene sediments at a later time. The samples from Zell are quite variable, perhaps due to weathering or intrusion. The two samples from Oberbipp that show closed system behaviour fall at low levels of IcPD, as expected given their Holocene age.

In summary, this first IcPD data from fossil worm granules indicates that for some samples this biomineral does retain closed system protein as far back as the Early Pleistocene. The relatively high variability in some sites may be due to multiple species being analysed, reworking / intrustion, or due to a less conservative set of proteins being incorporated into the mineral due to its excretory purpose. The multi-crystalline structure of the worm granules (Mandera *et al.*, 2023) may also be more susceptible to weathering than the denser calcite of opercula and slug plates. Combined with the relatively high levels of non-closed system behaviour evident in the worm granules, and the high potential for intrusion, this preliminary dataset indicates that this biomineral may not be ideal for high resolution studies. Despite this, there remains a signal of age in the worm granule dataset. Assuming the same effective diagenetic temperatures experienced at all the sites, for sites where age interpretation is possible, the relative age order predicted by the worm granules is therefore (oldest to youngest): Irchel Ebni ≈ Albishorn Bürglen ≈ Irchel Hochwacht ≈ Irchel Steig ≈Irchel Hasli Bräm ≈ Irchel Hasli 2018/19 > Hungerbol 2 ≈ Hungerbol 1 ≫ Sous-Terre 2 ≫ Petit Saconnex ≈ Niederweningen 2018 ≈ Nuolen ≈ Zell ≫ Oberbipp. This fits with the general stratigraphic order of sites, which is a positive sign for the geochronological potential of worm granules, despite the high levels of variability observed.

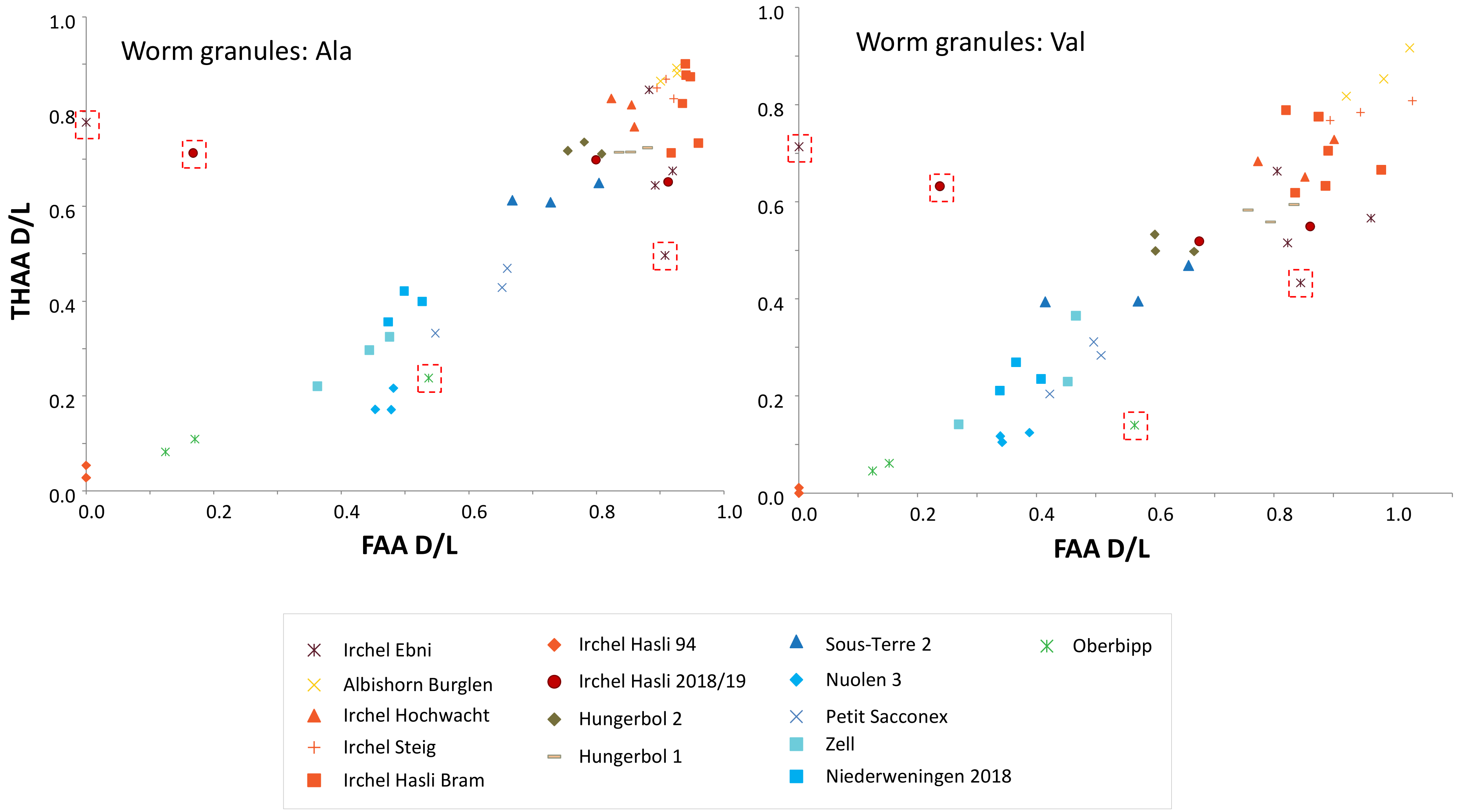

Figure 7: THAA D/L vs FAA D/L for Ala and Val in worm granules from Switzerland. One sample from Oberbipp, one sample from Irchel Hasli 2018/19 and two samples from Irchel Ebni fall further from the likely trendline for closed-system behaviour, so are outlined in a red-dashed square. The samples from Irchel Hasli 94 are likely to be modern intrusions.

4. Conclusions: implications for AA geochronology & potential for the Swiss Quaternary

The amino acid data from these samples shows that age discrimination is possible between the Quaternary sites from the Swiss Plateau using this technique in six different biominerals: *Bithynia* opercula, shell fragments from *Fruticola*, *Arianta* and *Cepaea*, slug plates and worm granules. This significantly widens the types of material that can be used for amino acid geochronology, and therefore the palaeoenvironments that can be examined. This dataset shows a clear need for additional samples per horizon to be undertaken for certain biominerals in order to fully assess their natural variability, and hence their temporal resolution.

A small number of samples did not show closed system behaviour, and therefore these individuals were not used to provide age interpretations. It is also apparent that amino acid dating must be undertaken with due regard for potential anthropogenic heating of the biominerals (such as that seen at the archaeological site of Abri Unterkobel), intrusion of younger material (as seen in the worm granule dataset) and signs of weathering on the shells (such as that which affected the *Arianta* from Hungerbol 2). While archive samples have produced very useful data, it is helpful to analyse material from sediment with a known processing history where possible.

The use of multiple amino acids is helpful in the generation of an overall IcPD aminostratigraphy. Interestingly the levels of temporal range and resolution differ between the biominerals, and this, combined with the lack of a single biomineral across all sites, means that a composite approach has been required in developing an aminostratigraphy for this region. In general the aminostratigraphy fits well with the independent evidence of age for the sites. The conjunction of the molluscan analyses (Thew, 2024) and the AA geochronology have led to some interesting new discoveries, which help to fill in some of the gaps in the Swiss Pleistocene chronology.

The AA analyses strengthened the lithostratigraphic and biostratigraphic picture for the Early Pleistocene deposits from the Irchel Plateau. The Ebni silts are oldest, while the HF deposits likely represent a single stratigraphic unit, despite some variation caused by weathering of some of the shell. The AA datas*et al*so confirmed biostratigraphic information from the molluscs that deposits sampled at Albishorn 2 are of a similar age to the HF.

Ecoteaux is the first site in Switzerland to be reasonably securely attributed to the Cromerian. Sous-Terre 2 and Montfleury were shown by the AA data to be of similar age, providing support to lithostratigraphic and molluscan evidence for an MIS 11 age for these two sites, making them the first that can be attributed to this period in Switzerland.

The AA data confirm that the deposits at Grandson and Nuolen are late Middle Pleistocene, in keeping with Grandson's link to the Rhine system and Nuolen's stratigraphic position within a Hochterrasse sequence. Petit Saconnex and WHO have a similar lithostratigraphic context and comparable molluscan assemblages, as well as AA data. Together with the data from Sous-Terre 2 and Montfleury, this dataset provides valuable new insights into the chronology of deposits in the Geneva area.

Despite strong lithostratigraphic and OSL evidence that the lake deposits at Thalgut are of Eemian age, both sets of samples produced IcPD values that seem to be older. While the possibility that the deposits may be older remains, the most likely scenario is one where all the sample material was heated at some point post-collection, probably to dry it.

The Holocene material from Oberbipp & Hauterive-Champréveyres provided some of the lowest levels of IcPD as expected, while the high values from some of the shells from Abri Unterkobel shows the importance of taking into account any anthropogenic heating of sediments when selecting samples for AA analysis.

This dataset therefore provides the first aminostratigraphy for the Swiss Plateau (lowland Switzerland north of the Alps), and the intra-crystalline protein decomposition (IcPD) in novel biominerals (slug plates and worm granules) exhibit useful age information, although it is recommended more samples are analysed per horizon for these taxa.

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Author contributions

Roles of the authors: GD led the NAGRA project studying the deckenschotter deposits from northern Switzerland, for which the molluscan analyses and IcPD dating form a part, and helped with sampling the Irchel sites. NT excavated, documented and sampled the Irchel sites and Hungerbol, collected shell material from Museums, specialists and previously studied sites, analysed all the molluscan assemblages and collated stratigraphic and dating information from the studied sites; DK excavated and sampled the Irchel sites and Hungerbol and provided new shell material from Zell. KP led the aminostratigraphic study; ST, SP & EN undertook the laboratory analyses. All authors were involved in writing the manuscript.

Data Availability

All amino acid data from this study will be made available through the NOAA repository upon final publication: https://www.ncei.noaa.gov/pub/data/paleo/aar/. For the purpose of open access a Creative Commons Attribution (CC BY) licence is applied to any Author Accepted Manuscript version arising from this submission.

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