Record of the end-Triassic mass extinction in shallow marine carbonates: the Lorüns section (Austria)

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Cover Picture: View of a part of the Lorüns quarry in Austria. Photo: Sylvain Richoz

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LINUS BRAKEBUSCH

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Abstract: The end-Triassic mass extinction (ETE) was one of the five big mass extinctions of the Phanerozoic and occurred ~201 Ma ago. Research agrees that the main triggering factor for the ETE was the eruptions of the Central Atlantic Magmatic Volcanic Province (CAMP), linked to the break-up of the supercontinent Pangaea. The large amounts of CO_2 and SO_2 released from the volcanic eruptions had a series of consequences such as climatic changes and ocean acidification, all possibly contributing to an extinction of a large number of taxa in the marine and terrestrial realm.

The Lorüns section constitutes a shallow-marine carbonate succession located in the Northern Calcareous Alps (NCA), Austria, and is a key section for studying the ETE because it records continuous sedimentation from the late Rhaetian to the Sinemurian. In this study, the Rhaetian Kössen Formation, the Schattwald Beds, and the Hettangian Lorüns oolite have been petrographically analysed. Geochemical analyses with laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) were also performed, mainly on the recovery facies from the Lorüns oolite. This study aims to offer a detailed description of the geological, geochemical and palaeoenvironmental conditions at Lorüns in the aftermath of the ETE and to compare the results with other Triassic-Jurassic boundary sections around the world.

The lack of calcareous fossils and the deposition of the siliciclastic Schattwald Beds during the "Extinction interval" together with the formation of coated grains in the post-extinction Lorüns oolite indicate that ocean acidification occurred in this area, especially affecting acid-sensitive organisms. Seawater was oxygenated during the early Hettangian. However, dysoxia occurred in the sediments during this period and is ascribed to the loss of biogenic sediment mixing due to the extinction of infaunal taxa. Analysis of the weathering proxies Si, Al, and Ti shows that weathering decreased continuously during the Hettangian. This could be explained by the marine transgression in the Lorüns area, a greater distance to the siliciclastic input zone, or because of a shift towards a less humid and hot climate after the extreme greenhouse conditions caused by volcanism around the ETE. Contrarily to the models from Hardie (1996) and Stanley & Hardie (1998), who propose an "aragonite" sea in the Late Triassic and Early Jurassic, the sea was found to be low-Mg calcitic at the time of deposition of the Schattwald Beds and Lorüns oolite. Triassic-Jurassic boundary sections in the Arab Emirates also imply a low-Mg calcitic sea, suggesting that the signal recorded at Lorüns was global, or at least Tethys-wide. Hence, the shift from an "aragonite" to "calcite" sea might have occurred earlier than previously believed.

Keywords: sedimentology, geochemistry, ooids, oolites, oncoids, oncolites, Triassic, Jurassic, Rhaetian, Hettangian, ocean acidification

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Subject: Bedrock Geology

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Det sen-Triassiska massutdöendet i Lorünssektionen i Österrike

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Sammanfattning: Det sen-Triassiska massutdöendet (STM) var ett av de fem stora massutdöenden i Fanerozoikum och inträffade för omkring 201 miljoner år sedan. Forskningen är enig om att utdöendet orsakades av vulkanutbrotten associerade med bildandet av den Centralatlantiska magmatiska provinsen (CAMP), som är kopplade till uppbrottet av superkontinenten Pangea. De omfattande vulkaniska utsläppen av CO₂ och SO₂ ledde till miljöpåverkan i form av klimatförändringar och havsförsurning, vilket i sin tur bidrog till att många arter i havet och på land dog ut.

Lorünsblottningen är en kalkstensavlagring från de Norra Kalkalperna i Österrike. Det är en viktig blottning för att studera det sen-Triassiska massutdöendet eftersom den representerar kontinuerlig sedimentation från sen rät till sinemur. I detta projekt har Kössen Formationen från rät, samt Schattwaldlagren och Lorünsooliten från hettang analyserats petrografiskt. Geokemiska analyser av framförallt de lager som avsattes direkt efter utdöendet utfördes genom laser-spektroskopi (LA-ICP-MS). Syftet med projektet är att ge en detaljerad beskrivning av de geologiska och geokemiska förhållandena samt miljön i Lorüns under återhämtningsfasen av STM och jämföra resultaten med andra likåldriga sektioner globalt.

Avsaknaden av kalkhaltiga fossil och avlagringen av de siliciklastiska Schattwaldlagren under STM tillsammans med bildandet av abiotiska karbonatkorn i Lorünsooliten tyder på att havsförsurning skedde i Lorüns. Särskilt påverkade av detta var syrakänsliga organismer. Havsvattnet var syresatt under hela återhämtningsfasen efter utdöendet. Under tidig hettang rådde syrefattiga förhållanden i sedimenten, vilket kan förklaras genom förlusten av bioturbation på grund av att infaunan dog ut. Vittringsproxys som Si, Al och Ti indikerar att vittringen minskade under hela hettang. Detta kan bero på att havsnivån steg, att avståndet till det siliciklastiska källområdet ökade eller på grund av att klimatet blev mindre fuktigt och varmt efter de extrema växthusförhållandena orsakade av vulkanism i samband med massutdöendet. I motsats till modellerna från Hardie (1996) och Stanley & Hardie (1998), som föreslog ett aragonitiskt hav i sen trias och tidig jura, var havet låg-Mg kalcitiskt i de sen-rätiska till tidig-hettangiska Schattwaldlagren och Lorünsooliten. Trias-jura gränsavlagringar från Förenade Arabemiraten visar också på ett låg-Mg kalcitiskt hav vilket tyder på att förhållandena i Lorüns var globala eller åtminstone förekommande över hela Tethyshavet. Övergången från ett aragonitiskt till kalcitiskt hav kan därför ha skett tidigare än vad man har trott tidigare.

Nyckelord: sedimentologi, geokemi, ooider, ooliter, onkoider, onkoliter, trias, jura, rät, hettang, havsförsurning

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1 Introduction

Current global warming and the associated severe extinction of different species around the world have led some authors to propose a contemporary mass extinction caused by humans (Cowie et al., 2022; Kolbert, 2014). The Anthropocene mass extinction has not occurred yet, but some researchers propose that it might happen within a few centuries (Barnosky et al., 2011) or is already ongoing (Thomas, 2017). To better estimate the impact and consequences of global climate change and a potential mass extinction, the five previous mass extinctions during the Phanerozoic can be investigated (Hautmann, 2012).

One of these mass extinction events is the end-Triassic extinction event (ETE), which occurred ~201 Ma ago (Korte et al., 2019), and is recorded in strata around the world (Lindström et al., 2021). Current research agrees that the main triggering factor for the ETE was the large eruptions of a Large Igneous Province (LIP) named the Central Atlantic Magmatic Province (CAMP), related to the break-up of the supercontinent Pangaea. This large event had a series of consequences including sea-level changes, marine anoxia, climatic changes, release of toxic compounds and ocean acidification, all possibly contributing to the extinction of a large number of taxa (Hautmann, 2012). There is still debate about the chain of events and tempo for this extinction (Lindström et al., 2021).

In this Master thesis, I investigated the Lorüns section, from the Lorüns quarry near Bludenz in Austria. This is a shallow-marine carbonate section from the Tethys deposited during the Late Triassic to the Early Jurassic period, without any significant gaps in deposition (Felber et al., 2015). To better study the recovery from the ETE, the Hettangian formation called Lorüns oolite, containing oolites and oncolites (Furrer, 1993), is of certain interest. During the Phanerozoic, ooid deposition was common in the direct aftermath of several mass extinction and smaller extinction events (Groves & Calner, 2004) like the Silurian Mulde and Lau events (Calner, 2005; Calner & Säll, 1999), the end-Permian extinction (Li et al., 2013; Li et al., 2015), or the ETE (Felber et al., 2015). Ooids are valuable palaeoenvironmental proxies for water energy, temperature, salinity and water depths because their microfabrics, mineralogy, abundance, and size reflect physical and chemical conditions of depositional environments in marine and non-marine settings (Flügel, 2010).

I performed petrographic, sedimentological, and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analysis on rocks from the Lorüns section. Petrographic and sedimentological studies enable interpretation of the depositional environment and relative sea-level changes, and LA-ICP-MS allows for geochemical assessment of elements, which can give information about the geochemistry of the seawater during the formation of the sediments. I have also prepared samples for $\delta^{13}C_{carb}$ -analysis.

My results are compared with the studies of Urban et al. (submitted) and Greiff (2021) from the Ghalilah Formation in the Arab Emirates. This ooidbearing formation was deposited during the Late Triassic and Early Jurassic (Maurer et al., 2008). Because the Ghalilah Formation was deposited during a similar time interval as the Lorüns section and both formations contain ooids, a comparison between the Lorüns section and the Ghalilah Formation is suitable to determine if the climatic signal recorded in Lorüns is regional or global. I conclude the report by discussing the ambiguity of the carbon isotope curves of earlier studies and highlight the importance of new $\delta^{13}C_{carb}$ measurements of the Lorüns section.

2 Background

2.1 The end-Triassic mass extinction (ETE)

2.1.1 The ETE and its biotic consequences

The end-Triassic mass extinction (ETE) was one of the five big mass extinctions during the Phanerozoic and occurred ~201 Ma ago (Todaro et al., 2018; Korte et al., 2019). 46.8 % of all marine genera became extinct between the Rhaetian and the Hettangian (Bambach et al., 2004). The conodonts, all but two ammonoid genera, 71 % of the articulate brachiopods and 40 % of the bivalves became extinct (Hautmann, 2012). Also reefbuilding organisms suffered huge losses and did not become fully re-established until 8-10 Ma after the extinction (Stanley Jr., 2006).

The ecosystems of terrestrial plant communities were perturbated during the ETE, but few taxa became extinct (Ash, 1986; Kelber, 1998; McElwain et al., 2009). Because of their great similarity the term 'Rhaetoliassic floras' has been used for the Rhaetian and Early Jurassic floras (Hautmann, 2012). van de Schootbrugge et al. (2009) noted a vegetation shift at the Triassic-Jurassic Boundary (TJB) in northwest Europe, where gymnosperm forests were replaced for a short time by fern and fern-associated vegetation. This shift is indicative of a disturbed ecosystem and can be coupled to the mass extinction event. Among the bigger animals, all crurotarsan archosaurs except the crocodylomorphs went extinct during the ETE (Stubbs et al., 2013).

2.1.2 The Jurassic system Global Stratotype Section and Point (GSSP) and its definit ion

The Global Stratotype Section and Point (GSSP) for the base of the Jurassic system is located at the Kuhjoch Pass in Tyrol, Austria and was defined in 2008 (Hillebrandt et al., 2013). The TJB is estimated to 201.36 ± 0.17 Ma, based on the first occurrence of the ammonite species *Psiloceras spelae tirolicum* (Schoene et al., 2010; Wotzlaw et al., 2014). This genus has a wide distribution, facilitating correlation with *Psiloceras* species for example in North America (Hillebrandt et al., 2013). Biostratigraphic correlation between different paleogeographic regions is also facilitated by the last appearance datum of the Rhaetian ammonoid *Christoceras marshi*, which marks the base of the extinction interval (Hillebrandt & Krystyn, 2009; Hille-

brandt et al., 2013). Very helpful for global correlations with Kuhjoch are the extremely rich marine fauna and microflora at the locality (Hillebrandt et al., 2013). Microfloral occurrence also facilitates crosscorrelation with terrestrial sections. The low diagenetic overprint permits the application of chemical proxies like δ^{13} C or Total Organic Carbon (TOC) at Kuhjoch. When analysing $\delta^{13}C_{org}$ across the TJB at the Kuhjoch locality two distinct negative excursions are recorded at the western part of it (Hillebrandt et al., 2013) (Fig. 1). The initial negative carbon excursion (CIE), called "initial CIE" (Hesselbo et al., 2002) or "marshi CIE" (Lindström et al., 2019) occurs at the same time as the ETE in the Rhaetian and shows a sharp decrease in $\delta^{13}C_{org}$ (Hillebrandt et al., 2013; Pálfy et al., 2021). A prolonged negative carbon isotope excursion with decrease in $\delta^{13}C_{org}$, called the less "main al., CIE' (Hesselbo et 2002) or "spelae CIE" (Lindström et al., 2019), is observed further up in the Rhaetian (Hillebrandt et al., 2013). These $\delta^{13}C_{org}$ -excursions appear in many sections around the world and can therefore be used as global correlation tools (Korte et al., 2019; Pálfy et al., 2021) (Fig. 2).

2.1.3 The Central Atlantic Magmatic Province (CAMP) and its origin

Research agrees that the main triggering factor for the ETE was the eruptions of the Central Atlantic Magmatic Volcanic Province (CAMP), which likely were linked with the break-up of the supercontinent Pangaea and the opening of the central Atlantic (Lindström et al., 2021; Peace et al., 2020). The CAMP magmatism was of tholeiitic basaltic composition and its remnants are today found in South and North America, Africa, and Europe (Lindström et al., 2021) (Fig. 3). In total, the surface area of CAMP-magmatic rocks covered more than ~10 million km², which corresponds to an original volume of more than 3 km³ of magmatic rocks (Marzoli et al., 2019). The peak magmatic activity of the CAMP occurred between 201.6 and 201.3 Ma and is synchronous with the ETE (Blackburn et al., 2013; Davies et al., 2017). Magmatism lasted discontinuously until ~196 Ma in some areas of the CAMP (Marzoli et al., 2019).







Fig. 2. Correlations between $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ -curves around the Triassic-Jurassic Boundary (TJB) in shallow marine carbonate sections around the world. Highlighted in red is the initial CIE, highlighted in blue is the main CIE and highlighted in green are positive $\delta^{13}C$ -shifts. (Pálfy et al., 2021)

The origin of the CAMP is debated and both a supercontinent rift-related magmatism and a mantle plume have been proposed as triggering factors for the magmatism (Marzoli et al., 2019). After analysis of geochemical and thermometric data (Callegaro et al., 2013; Herzberg & Gazel, 2009; Whalen et al., 2015), a classical mantle plume origin for the CAMP was ruled out due to unsuitability in all these categories (Marzoli et al., 2019). Burov & Gerya (2014) proposed a mantle-plume, which rises under an already extending plate as the origin of the CAMP. This model is supported by the asymmetric distribution of magmatic rifts and amagmatic horst structures (Burov & Gerya, 2014) and paleomagnetic reconstructions (Ruiz -Martínez et al., 2012). For explaining the nearsynchronous melting over the entire CAMP-province, McHone (2000) and Coltice et al. (2007) proposed scenarios based on continental thermal insulation under Pangaea. Heron & Lowman (2010) and Heron & Lowman (2014) suggested that continental insulation is not the primary influence of supercontinents on mantle temperature and Whalen et al. (2015) point toward a greater influence of inherited fertile mantle on the CAMP. Kaiho et al. (2022) performed coronene index measurements at the sedimentary sections at Kuhjoch and St Audrie's Bay. Coronene index is a proxy for heating temperature (Kaiho et al., 2022). Due to lower indices as compared to the plume-related end-Permian event, they interpreted the volcanic style of the CAMP to be rather of supercontinent rift-related type.

2.1.4 Emissions from the CAMP and their impact

The main consequences of volcanic eruptions are the large emissions of volcanic volatiles in shape of water vapor, carbon dioxide, methane, sulphur dioxide, halogens and their compounds (Lindström et al., 2021).

These compounds alter the global atmospheric chemistry and influence radiative forcing (von Glasow et al., 2009). Unfortunately, traces from volcanogenic degassing from the CAMP are sparse, but because similar effects were observed from historical eruptions, it is likely that the CAMP emplacement caused many of the environmental changes associated with the TJtransition (Robock, 2002; Thordarson & Self, 2003).

Carbon dioxide (CO₂) has an atmospheric residence time of several thousands of years (Archer, 2005) and is one of the most common greenhouse gases emitted by volcanism (Lindström et al., 2021). Capriolo et al. (2020) estimated the total CO₂ emissions of the CAMP to 10^5 Gigatons. This corresponds to 7 Gt per year during the main volcanic pulses, which could have led to a global temperature increase of more than 4 °C (Capriolo et al., 2020; Landwehrs et al., 2020). Therefore, CAMP volcanism was a likely cause for the disruption of the end-Triassic carbon cycle (Lindström et al., 2021).

Methane (CH₄) is among the highest impact global greenhouse gases and was generated or remobilised in sedimentary basins due to magma-sediment interaction (Capriolo et al., 2021). The main part of the methane was reintroduced into sedimentary host rocks or discharged into the surface system during CAMP activity, with a minimal amount trapped within quartz-hosted fluid inclusions. When released into the atmosphere, methane similarly to CO_2 contributed to the global warming during the ETE. Because of its ¹³C-depleted signature, sedimentary organic methane, when injected into the carbon cycle, was a potential reason for the negative carbon-isotope shifts in the sedimentary record (Capriolo et al., 2021; Ruhl et al., 2011).

Sulphur dioxide (SO₂) can be released from direct and thermogenic degassing during basaltic volcanism (Callegaro et al., 2014; Iacono-Marziano et al.,



Fig. 3. Palaeogeographic map of Pangaea showing the extent of the Central Atlantic Magmatic Province (CAMP). Red circle highlights the location of the Northern Calcareous Alps (NCA). Modified from Lindström et al. (2021).

2017; Jones et al., 2016; Self et al., 2008). However, because it is not possible to study magmatic traces with sulphur isotopes in sedimentary records, it is difficult to trace the sulphur emissions to the atmosphere from the CAMP (Lindström et al., 2021; Newton & Bottrell, 2007). Sulphur has a residence time of a few weeks in the troposphere but several years in the stratosphere (Lindström et al., 2021; Robock, 2000). The impact of sulphur in the troposphere is local because of a short residence time, and affects ecosystems by causing acid fallout, which leads to poisoning of continental ecosystems and vegetation damage (Lindström et al., 2021). If sulphur reaches the stratosphere the impact is global, as has been demonstrated for historical eruptions (Grattan & Pyatt, 1999; Grattan, 2005). Sulphates act as aerosols and reflect the incoming solar radiation, which leads to a cooling of the troposphere and heating of the stratosphere (Lindström et al., 2021). If the volcanic pulses are short-lived and intense, this may lead to temperature drops of 5-6 °C (Landwehrs et al., 2020).

Kaiho et al. (2022) discovered that SO₂ gas forms more at lower temperatures of volcanism, while CO₂ gas forms more at higher temperatures of volcanism. Hence, they proposed that the early CAMP pulses of lower temperature induced explosive eruptions with ejections of SO₂ and water vapor into the atmosphere. This led to <1000 years of global cooling which caused or contributed to the terrestrial and marine extinction of the ETE. The global cooling was followed by global warming during >100 000 years as the CAMP-volcanism increased in temperature, favouring CO₂-emissions over SO₂-emissions. During the warming event the eruptive style of the volcanos changed to be less explosive with less phreatic-volatile release, as compared to the previous volcanic phase.

Halogens can form both from magmatism and from contact metamorphism of especially evaporitic sediments (Svensen et al., 2009). By participating in complex radical reactions in the troposphere and inducing ozone depletion in the stratosphere these compounds might cause environmental disruption (von Glasow et al., 2009). If ozone layer depletion played a major part in the ETE remains to be investigated (Lindström et al., 2021). Due to its high toxicity, Fluorine (F) might also directly kill off organisms around volcanic areas (McHone, 2003).

Mercury (Hg) is a genotoxic heavy metal (Nagajyoti et al., 2010), and has primarily been released to the atmosphere in pre-industrial times through volcanic activity (Lindström et al., 2021). Hg anomalies are important for linking CAMP volcanism to the ETE (Percival et al., 2017). Lindström *et al.* (2021) observed Hg anomalies before the ETE, indicating that CAMP activity began before the marine extinction. The release of Hg in the atmosphere has also been proposed as a killing agent in the ETE, because it coincides with occurrences of abnormal fern spores (Lindström *et al.* 2019).

2.1.5 Marine anoxia

Wignall (2001) proposed that marine anoxia developed as a consequence of the global warming resulting from volcanogenic CO_2 -emissions during the ETE. He argued that these emissions caused a decrease in the equator-to-pole temperature gradient leading to a reduced thermohaline circulation and increased ocean stratification. Furthermore, the rapid rise of atmospheric pCO_2 would increase the amount of weathering and delivery of bio-limiting nutrients to the oceans, leading to eutrophication and expansion of oxygen minimum zones (OMZ) (Meyer & Kump, 2008). Due to these large environmental consequences, the impact of marine anoxia on the ETE and its recovery, has been a subject for research.

McRoberts et al. (2012) observed epifaunal and shallow burrowing bivalve taxa not indicative of dysoxic conditions in the extinction interval in Austrian sections. The large amount of organic matter deposited during the extinction at the Kuhjoch locality was interpreted to have formed from terrestrial rather than marine sources (Ruhl et al., 2010). Geochemical analysis of the Kendlbachgraben section in Austria showed that oxygen-depleted bottom water conditions only were present during brief intervals of the ETE and did not play a fundamental role in the extinction (Pálfy & Zazjon, 2012).

Based on investigations of core material from Germany and Luxembourg, Richoz et al. (2012) discovered that anoxia appeared in the Tethys Ocean after the ETE. They argued that anoxia in combination with repeated hydrogen sulphide poisoning might have delayed marine biotic recovery during the Early Jurassic. In Britain, conditions were dysoxic during the recovery period from the extinction in the earliest Jurassic, especially in deeper waters (Atkinson & Wignall, 2019). The fauna recovered quickly in shallow water settings (<0.7 Ma) and slightly slower in deep water settings (>2 Ma). A possible scenario for the ETE could be that marine organisms diversified in the best oxygenated shallow-water settings and populated the more dysoxic deep-water settings during intervals of improved oxygenation (Atkinson & Wignall, 2019).

To summarise, repeated intervals of anoxia existed during and after the ETE, but the extent and impact of anoxia varied between different places. Research agrees that anoxia was no main killing agent for the ETE. However, it could delay biotic recovery in some places.

2.1.6 Ocean acidification

Ocean acidification is the process where seawater pH decreases due to oceanic uptake of CO_2 (Hautmann, 2012; McRoberts et al., 2012). During the ETE, volcanogenic emissions of CO_2 and SO_2 were taken up into the ocean and reduced CaCO₃ saturation of the seawater (Hautmann, 2004). This possibly led to a complete CaCO₃ undersaturation of the world's oceans over a period 20-40 ka, provided that the emissions were short-lived (Berner & Beerling, 2007). The undersaturation is recorded in marine strata around the world, by a global carbon gap above the extinction horizon (Hautmann, 2012).

This biocalcification crisis led to an increased extinction risk for calcareous-walled taxa (Hautmann, 2012). For the shell-bearing biota, the ETE favoured the development of organic-walled phytoplankton (van de Schootbrugge et al., 2007) and agglutinated foraminifera (Clémence et al., 2010), while calcareouswalled taxa became less abundant. Calcitic or noncalcareous bivalves were clearly more common than bivalves with more soluble aragonitic shells (Hautmann et al., 2008). Hypercalcifying bivalve taxa declined during the mass extinction, due to the increased energy required for biomineralisation during times of reduced CaCO₃. required for biomineralisation during times of reduced CaCO₃.

2.2 Ooids

2.2.1 Definition and types of ooids

According to Flügel (2010) ooids are "spherical and egg-shaped carbonate or non-carbonate coated grains exhibiting a nucleus surrounded by an external cortex, the outer part of which is concentrically smoothly laminated". Modern calcareous ooids consist of either aragonite or calcite and most of them have a size smaller than 2 mm. Ancient calcareous ooids are always calcitic, if they are not silicified or dolomitised, because aragonitic ooids will be replaced by calcite (calcitisation) or dissolved completely during diagenesis (Tucker, 2001). The remaining holes that are left from the dissolved aragonitic ooids are called oomoulds and might be left empty or filled with calcite cement as diagenesis progresses. If the ooids are rockforming the resulting rock is called an oolite (Flügel, 2010).

Ooid formation is still debated and to date several different models have been proposed for their formation (Varkouhi & Ribeiro, 2020) including accretion of fine particles around a nucleus while agitating on a soft substrate (Mei & Gao 2012), abiotic precipitation from surrounding supersaturated water around a nucleus (Duguid et al. 2010) and organomineralisation of a surface biofilm (Batchelor et al., 2018; Diaz et al., 2014; Diaz et al., 2017; Li et al., 2017). However, most research agrees that a majority of the ooids form in shallow waters, which are regularly agitated by waves and currents over a long period of time (Flügel, 2010). Environments with minimal siliciclastic input and warm temperatures are also favourable for ooid formation. Flügel (2010) identified five requirements for depositional environments to permit the formation of carbonate ooids: the presence of nuclei, bottom agitation to move grains, a source of supersaturated water, a process of water renewal, and minimal amount of grain degradational processes.

Ooids can be divided into three different groups based on the microfabric of their cortex (Flügel, 2010) (Fig. 4). Concentric ooids have concentric laminae of tangentially arranged crystals and usually occur in high-energy settings. Radial ooids have laminae which consist of radially arranged crystals and occur in lowenergy settings. Micritic ooids can either have a lamination and crystals with random arrangement or show no lamination due to a ubiquitous micritisation of the cortex (Urban et al., submitted). They are common in shallow-marine settings (Flügel, 2010). Coated grains whose original cortices were completely obliterated by bacteria or endolithic organisms in post-formation stages are called micritised ooids (Urban et al., submitted). Ooids can also be divided according to the thickness of their cortex. In this classification, differences are made between superficial ooids (Carozzi, 1957) where the thickness of the cortex is less than half of the diameter of the ooids and 'normal' ooids (Flügel, 2010), where the thickness of the cortex equals or exceeds half the diameter of the ooid.

	Microfabric of the cortex	Mineralogy	, modern examples	Environment
Concentric (tangential) ooids	Concentric laminae consisting of tangentially arranged crystals whose long axes are aligned to the surface of the laminae. High microporosity	Aragonite:	Bahamas, Yucatan, Abu Dhabi, Persian Gulf	Very shallow, warm low- latitudinal seas; <i>common in</i> <i>high-energy settings</i>
			(Great Salt Lake/Utah)	Lacustrine-hypersaline
		Low-Mg calcite: Caliche ooids*		Terrestrial
Radial (radial-fibrous) ooids	Laminae consisting of radially arranged crystals; long crystal axes perpendicular to the laminae surface	Aragonite:	Persian Gulf, Great Barrier Reef, (Yucatan, Shark Bay, Mediterranean)	Shallow marine, <i>common in low-energy settings</i>
			Gulf of Aqaba	Sea-marginal hypersaline pool
			Great Salt Lake/Utah	Lacustrine-hypersaline
		Mg-calcite:	(Baffin Bay/Texas)	Marine-hypersaline
		Calcite and	Low-Mg calcite: e.g. Cave pearls*	Non-marine
Micritic (random) ooids	Laminae composed of randomly arranged microcrystalline crystals or Laminae obliterated or absent, due to a pervasive micritization of the cortex	Aragonite:	Bahamas	Shallow-marine

Fig. 4. Palaeogeographic map of Pangaea showing the extent of the Central Atlantic Magmatic Province (CAMP). Red circle highlights the location of the Northern Calcareous Alps (NCA). Modified from Lindström et al. (2021).

2.2.2 Ooids as sedimentological proxies

Due to their specific environmental requirements, ooids can be applied as sedimentological proxies for paleoenvironmental analysis. Water energy levels and transport processes can be estimated by determining the amount of autochthonous ooids (deposited at the place of origin) and allochthonous ooids (transported to the place of deposition) (Flügel, 2010). Distinguishing between concentric, radial, and micritic ooids can also be useful for analysing water energy levels. Because the shape and microfabrics differ between freshwater and marine ooids, ooids can be used as salinity proxies (Flügel, 2010). Plee et al. (2008) noted that ooids can be used for estimating palaeowater-depth.

The appearance and composition of ooids can be used for indicating sea-level fluctuations, because these are affected by the depositional setting and water circulation (Flügel, 2010). Ooids are also good indicators for paleoclimate and palaeoceanography. Their occurrence is related to warm waters with high salinities (Lees, 1975), usually located in the tropics or lower subtropics, but not at or very near the equator (Flügel, 2010). The palaeoclimate can be studied by analysing the diagenetic style of ancient ooids (Flügel, 2010). For example, arid climate is coupled to few early meteoric cements while humid climate is coupled to more abundant meteoric cements (Hird & Tucker, 1988).

Ooidal cortex mineralogies can be used as a proxy for ancient seawater chemistry because their mineralogy mainly depends on the Mg/Ca ratio of the seawater (Varkouhi & Ribeiro, 2020). High-Mg calcite and aragonitic ooids form when Mg/Ca ratios in seawater are above a threshold of 2 (Ries, 2010; Stanley & Hardie, 1998, 1999; Stanley, 2006) while calcite ooids are precipitated when the Mg/Ca ratios in seawater are lower (Varkouhi & Ribeiro, 2020). This has particularly been used for determining the shifts between calcite and aragonite seas. Previously, concentric ooids were considered to be calcitic and radial ooids aragonitic (Sandberg, 1975), but this view has turned out to be too simplistic (Urban et al., submitted).

2.2.3 Cortoids, oncoids and peloids

Other coated grains frequently encountered in this study are cortoids, oncoids, and peloids (*Fig.* 5). Cortoids are bioclasts, ooids, lithoclasts and peloids, whose periphery displays a 'micrite envelope' (Flügel, 2010). A 'micrite envelope' is a circumgranular micritic rim around carbonate grains. Modern envelopes consist of aragonite or high-Mg calcite, and commonly occur around skeletal grains or ooids (Flügel, 2010). The size of the cortoid varies from <1 mm to a few centimetres.

Oncoids are, according to Flügel (2010), "unattached, rounded, mm- to cm sized, calcareous or non-calcareous nodules that commonly exhibit a micritic cortex consisting of more or less concentric and partially overlapping laminae around a bio- or lithoclastic nucleus". They commonly occur in limestones and marly sediments and can be distinguished from cortoids by the greater thickness of the micritic coatings and the frequency of preserved cyanobacteria, algal, or foraminiferal structures (Flügel, 2010). In contrast to ooids, oncoids are usually larger and have more irregular laminae. Ancient oncoids commonly consist of calcite, which sometimes is combined with mixtures of the minerals in proximity to the oncoids (Flügel, 2010). The mixtures could consist of clay minerals, quartz, and organic matter. Oncoids can form for example by trapping of fine-grained sediment on the surface of vanished microbial or algal felts, by microbially induced carbonate precipitation, by calcification of microbial or algal filaments, or from remains of skeletal microbes, calcareous algae or cyanobacteria (Flügel, 2010). They usually have a size from <1 mm to a few decimeters. A limestone consisting of more than 50 % oncoids is called an oncolite.

Peloids are small micritic grains which are subrounded, spherical, ovoid or irregular in shape (Flügel, 2010). They are characterised by a small size between 0.10 and 0.50 mm and their lack of internal structures. The composition of modern marine peloids is high-Mg -calcitic and/or aragonitic and they can form biotically, by the reworking of mud and grains, by alteration of grains, or in-situ (Flügel, 2010).

PELOIDS d o o o		0 0 0	Small micritic grains, commonly without internal structure. Subrounded, spherical ovoid or irregular in shape. Size between <0.02 and about 1 mm, commonly 0.10 to 0.50 mm.		
	CORTOIDS		Rounded skleletal grains and other grains covered by a thin micrite envelope. Boundary between the central grain and the envelope indistinct. Size between <1 mm to a few centimeters.		
GRAINS	ONCOIDS		Large and small grains consisting of a more or less distinct nucleus (e.g. a fossil) and a thick cortex formed by irregular, non-concentric, partially overlapping micritic laminae. Laminae may exhibit biogenic structures. No tendency to increase sphericity during growth. Size from <1 mm to a few decimeters.		
COATED	OOIDS	•	Spherical or ovoid grains, consisting of smooth and regular laminae formed as successive concentric coatings around a nucleus. Laminae may exhibit tangential and radial microfabrics. Size between 0.20 and about 2 mm, commonly between 0.5 and 1 mm.		

Fig. 5. Peloids and different types of coated grains and their definitions. (Flügel, 2010)

2.3 Major and trace elements for the LA-ICP-MS and their use as proxies

With LA-ICP-MS analysis, I analysed the quantities of several different elements, which could be used for palaeoenvironmental reconstruction. Here, I will give a short introduction to these elements.

Magnesium (Mg) is an important constituent of the minerals calcite and aragonite (Tucker, 2001). Mg readily substitutes into the hexagonal calcite structure, while this substitution is less common in the aragonite crystal structure (Flügel, 2010). Therefore, the amount of magnesium (Mg) is measured in LA-ICP-MS for verifying the mineralogy of ooids. According to Stanley & Hardie (1998) high-Mg calcite contains >4 mol % MgCO₃ while low-Mg calcite contains <4 mol % MgCO₃. Aragonite contains very low mol % MgCO₃ (Flügel, 2010).

Strontium (Sr) easily substitutes for Ca in aragonite during diagenesis, because strontianite (SrCO₃) is isostructural with aragonite (Pingitore Jr. et al., 1992). In calcite, which has a different crystallography than aragonite, this substitution is less common (Flügel, 2010). Hence, it is possible to interpret the original mineralogy of ooid cortices by measuring the amount of Sr (Li et al., 2013). Aragonitic ooids have Sr values around 8000-10000 ppm if they are precipitated from seawater (Tucker, 1985), while calcite contains less Sr (Flügel, 2010). In ancient limestones Sr values are usually around a few 100 ppm. This is mainly because of Sr-loss during neomorphic processes like transformation of aragonite into calcite, repeated dissolution-precipitation processes and recrystallisation (Flügel, 2010). Aragonite recrystallised to calcite still retains a higher amount of Sr than minerals directly deposited as calcite (Flügel, 2010). Another reason for the low Sr values in ancient limestones is because most late sparry calcite cements are precipitated from meteoric and meteoric-marine pore waters, containing low Sr (Tucker, 1985).

Phosphorous (P) in sediments is usually derived from dead phytoplankton reaching the sediment-water interface and fish scales and bones (Tribovillard et al., 2006). In anoxic waters, P generally returns to the water column, while Fe in oxic waters limits the diffusion of P to the water column. P is also a bio-limiting nutrient (Flügel, 2010), which might be used for tracing nutrient-rich water.

Barium (Ba) occurs in marine sediments mainly in detrital plagioclase crystals and as barite (BaSO₄) (Bishop, 1988; Rutsch et al., 1995) but the mechanisms for the formation of authigenic barite in surface waters are not fully understood (Tribovillard et al., 2006). Ba readily replaces Mg and Ca because they are in the same column of the periodic table. Biogenic Ba and barite have been proposed as proxies for palaeoproductivity because of the apparent relationship between the abundance of biogenic barite and organic matter and its behaviour as a refractory element in sediments with no sulphate reduction (Sanchez-Vidal et al., 2005). Because Ba might migrate during early diagenesis in sediments with a high organic matter flux, it is best used as a palaeoproductivity proxy in marine sediments deposited in areas of low to moderate productivity (Tribovillard et al., 2006).

Zinc (Zn) is usually depleted in surface water and is required for biological activity by eukaryotes (Bruland, 1980; Vallee & Auld, 1993; Zhao et al., 2014). It binds strongly to organic matter, might be enriched in marine sediments, and is released to pore waters by aerobic or anaerobic remineralisation of organic matter (Algeo & Maynard, 2004; Bruland, 1989; Morse & Luther, 1999). Siderite and magnetite might act as sinks for Zn during bacterial reduction (Cooper et al., 2000; Labrenz et al., 2000; Parmar et al., 2001), while Zn is not preferably incorporated in pyrite.

Manganese (Mn) plays a prominent role in the transfer of trace metals from the water column to the sediment (Tribovillard et al., 2006). The element displays an active biogeochemical cycle across redox boundaries below, at or above the sediment-water interface, due to the difference in solubility between the soluble Mn(II) and solid Mn(IV) species (Canfield et al., 1993). However, its applicability as a redox proxy is debated (Algeo & Maynard, 2004; Calvert & Pedersen, 1993; Takahashi et al., 2014) Mn can be used for assessing diagenetic alteration (Li et al., 2013). The Mn concentration in primary calcite and aragonite is usually <50 ppm, while the Mn concentration in secondary carbonate mineral phases formed under reducing conditions can contain much higher Mn concentrations.

Uranium (U) usually forms soluble carbonate complexes in oxic seawater at intermediate to high pH (Cumberland et al., 2016; Endrizzi & Rao, 2014; Morford & Emerson, 1999) and its transport from the photic zone to bottom waters and sediments is mainly controlled by the dissolved oxygen concentration and flux of organic matter (McManus et al., 2005; McManus et al. 2006). The CO_3^{2-} -content in the water controls the U-carbonate complexation in more detail (Keul et al., 2013). Remobilisation of U occurs if sedimentary redox conditions fluctuate frequently, while enrichment of U occurs at different redox potentials than other redox-sensitive elements like Mo (Algeo & Maynard, 2008). Increasing Ca and Dissolved Inorganic Carbon (DIC) concentrations can lead to decreasing reduction rates of U in sedimentary pore waters (Ulrich et al., 2011). Due to its versatile elemental properties U is applicable as a chronometer and as an indicator of past ocean anoxia and carbonate ion concentrations (De Carlo et al., 2015; Hamelin et al., 1991; Shen & Dunbar, 1995).

Vanadium (V) has various oxidation states and is part of enzymes and therefore an essential nutrient for phytoplankton in the photic zone (Moore et al., 1996; Nalewajko et al., 1995). pH and redox conditions determine the oxidation state of V, and V can be used as a tracer for biogeochemical processes in the water column and the sediments (Wanty & Goldhaber, 1992). V can be used as a proxy for anoxia and past oxic-to-suboxic transitions if it is used in combination with other trace elements (Smrzka et al., 2019; Wenger & Baker, 1986).

Molybdenum (Mo) is present in oxic seawater as molybdate (MOQ_4^2) and is mainly transferred from the water column to sediments via diffusion and absorption onto iron and manganese oxides, but also by binding to organic matter (Piper & Perkins, 2004; Zheng et al., 2000). Molybdate is enriched in sediments in the presence of dissolved sulphide, which impedes efficient Mo accumulation under denitrifying conditions (Helz et al., 1996; Helz et al., 2011; Piper & Perkins, 2004; Vorlicek et al., 2004). Moaccumulation in sediments is favoured in euxinic basins (Herrmann et al., 2012; Neubert et al., 2008).

Rhenium (Re) shows conservative behaviour in the oceans and is delivered to the oceans primarily by rivers (Anbar et al., 1992; Colodner et al., 1993). Diffusion mainly governs the Re input to the sediment from bottom waters (Colodner et al., 1993). Due to its low crustal content, high redox sensitivity and preservation potential during sedimentation and burial (Crusius & Thomson, 2003; Crusius et al., 1996; Koide et al., 1986; Morford & Emerson, 1999) Re is more enriched in reducing sediments than most other elements. These element properties make Re a reliable proxy for anoxic conditions (Smrzka et al., 2019).

Rare Earth Elements (REE) are a group of elements with identical outer shell configuration which makes them behave similarly in chemical reactions (Smrzka et al., 2019). Cerium (Ce) and Europium (Eu) can have various redox states, but all other REEs are trivalent (3+). REEs can be used for tracing biogeochemical processes and for reconstructing ancient environments after they have been normalised to a reference standard (Smrzka et al., 2019; Zwicker et al., 2018). The REEs can be divided into three different groups based on atomic weight: the Light Rare Earth Elements (LREE), the Middle Rare Earth Elements (MREE), and the Heavy Rare Earth Elements (HREE) (Smrzka et al., 2019). In seawater HREEs are enriched, Ce shows negative anomalies while Yttrium shows positive anomalies after (Y) shalenormalisation. The cause of HREE enrichment is that HREE elements form stable carbonate complexes in seawater, while LREEs get absorbed onto organic particles which removes them from the solution (Himmler et al., 2013). REEs and Y are useful for indicating redox conditions (German & Elderfield, 1990), relative water depths (Piepgras & Jacobsen, 1992), early diagenetic processes (Haley et al., 2004), microbial activities (Takahashi et al., 2005; Takahashi et al., 2007), and silicate contamination (Li et al., 2017).

Lithium (Li) enters the ocean with fluxes from continental weathering and hydrothermal activity (Hathorne & James, 2006; Misra & Froelich, 2012), and can be captured in secondary mineral formation during alteration of the oceanic crust and by incorporation into marine sediments (Chan & Edmond, 1988; Chan et al. 1992; Chan et al., 2006; Hathorne & James, 2006; Stoffyn-Egli & MacKenzie, 1984). Together with Al and Ca it can at some localities be applied as a proxy for continental material influx due to changes in the continental weathering (Kovács et al., 2020; von Strandmann et al., 2019).

Titanium (Ti) is a detrital element proxy (Kryc et al., 2003). It can be used together with Al (Al/Ti ratio) as a proxy for particle flux.

Aluminium (Al) usually has little ability to move in sediments during diagenesis, which makes it a useful indicator of the aluminosilicate fraction of the sediments (Brumsack, 1989; Calvert & Pedersen, 1993; Morford & Emerson, 1999; Piper & Perkins, 2004) or the amount of clay minerals (Pálfy & Zazjon, 2012). Al content is also used to normalise traceelement concentrations (Calvert & Pedersen, 1993).

Silicon (Si) is a constituent of silicate rocks, whose weathering is a dominant control on the natural carbon cycle on seasonal to multi-millennial timescales (von Strandmann et al., 2019). Together with Al it represents the amount of siliciclastics in rocks (Pálfy & Zazjon, 2012).



Fig. 6. Overview of the Late Triassic stratigraphy of the NCA. The whole area was a carbonate platform with shallow water carbonates, reef deposits, slope deposits and pelagic carbonates. (Kovács et al., 2020). The approximate position of the Lorüns quarry is indicated with a black dot.

3 Geological setting

3.1 Tectonics and palaeogeography

The Northern Calcareous Alps (NCA) consist of thrust sheets which contain carbonate sediments deposited between the Late Permian and Late Cretaceous (Mandl, 2000) (*Fig.* 3). It is classified as fold-and thrust belt extending from the Swiss-Austrian border to the Vienna basin, with a length of 500 km and a width of 20 to 50 km (Channell et al., 1990; Granado et al., 2018; Mandl, 2000;). The Lorüns quarry belongs to the Lechtal Nappe of the Bajuvaric nappe group (Furrer, 1993; Mandl, 2000). This group is the lowermost of the Bajuvaric, Tyrolic and Juvavic Nappe Stack.

Rifting and spreading of the Tethys Ocean during the Permian and Triassic formed a passive continental margin, where deposition of the sediments of the NCA occurred (Mandl, 2000) (*Fig.* 6). The eastern NCA experienced a transgression during the latest Carnian which led to the development of carbonate platforms. Some of these platforms, like the Dachstein platform, grew in a cyclical way and shifted from an open platform setting to a rimmed platform configuration in the Norian period. During the middle-late Rhaetian, these carbonate platforms were affected by extensional tectonics, related to the opening of the central Atlantic, and formed interplatform peritidal environments (Mandl, 2000; McRoberts et al., 1997). Terrigenous sediment influx during the Rhaetian reduced the area of these platforms (Mandl, 2000). Shallow-water carbonate production ceased during ETE due to the carbonate dissolution following the biotic crisis and subsequent ocean acidification (Pálfy et al., 2021). During the Early Jurassic the Austroalpine shelf drowned and synsedimentary faulting occurred (Mandl, 2000). This led to the deposition of crinoidal and ammonoid limestones above the former carbonate platforms.

3.2 Stratigraphy

The samples for this study were taken from Late Triassic and Early Jurassic formations of the Lorüns quarry in Austria. The Lorüns quarry is located near the town of Bludenz in Austria (N47°08'12.0''/E50'47.0'') (Felber et al., 2015) (*Fig.* 7a). Samples were taken from the Kössen Formation, the Schattwald Beds, the Lorüns oolite, the Hierlatz Limestone, and the Adnet Limestone (*Fig.* 7b., *Fig.* 8).



b)

Fig. 7. The Lorüns quarry near the town of Bludenz, Austria. a) Geographical overview of the investigated area. (Felber et al., 2015) b) Picture of the investigated section at the Lorüns quarry, with indicated stratigraphy. Cars for scale.

3.2.1 Kössen Formation

The Kössen Formation is a lower to late Rhaetian formation (Richoz & Krystyn, 2015) in the Northern Calcareous Alps, characterised by marly and bedded limestones interbedded with darker shales (Furrer, 1993; McRoberts et al., 1997). Lenses and nodules of lightercoloured massive limestones commonly occur inside the bedded limestones (Furrer, 1993). The Kössen Formation is fossil-rich and contains fossils and trace fossils from a large range of vertebrates and invertebrates. The formation, as developed on the western NCA, can be divided into five members of different regional extent. In ascending order these are: the Alplihorn Member, the Schesaplana Member, the Ramoz Member, the Mitgel Member, and the Zirmenkopf Member.

At the Lorüns quarry, the Kössen Formation has thickness of more than 60 m (McRoberts et al., 1997), but the sampling of this study only covered the topmost 4.9 m of this formation. This part of the formation is in Lorüns represented by the Zirmenkopf Member, which here is greyish and interbedded with green or red marly layers (Furrer, 1993). At the top of the Zirmenkopf Member the limestones and marls shift towards a red colour and coral fragments are common. The relatively pure carbonates and the presence of stenotopic invertebrates indicate deposition in shallow waters of normal marine salinity (McRoberts et al., 1997).

3.2.2 Schattwald Beds (Kendlbach Formation, Tiefengraben Member)

The Kendlbach Formation, Tiefengraben Member, deposited during the Rhaetian post-extinction to the middle Hettangian (Hillebrandt & Krystyn, 2009), is represented in Lorüns only by the Schattwald Beds (Felber et al., 2015). The Schattwald Beds directly overlay the Zirmenkopf Member and are characterised by interlayering of colourful silty shales, marls, limestones, and siltstones (Furrer, 1993). Intraclasts and remnants from the Zirmenkopf Limestone are common and the sediments are laminated (Furrer, 1993) and rarely show a gradation (this study).

The Schattwald Beds can be divided into two parts based on differences in facies (McRoberts et al., 1997). According to this study, the lowest 0.95 m of the Schattwald Beds at Lorüns are represented by the Lower Schattwald Beds, characterised by red, green, white, and black mudrocks and siltstones (McRoberts et al., 1997). Fossils are rare, some of the sediments oxidised, and quartz grains common, which indicate that the depositional environment might have been marginal marine with significant terrestrial influx (McRoberts et al., 1997).

The Upper Schattwald Beds cover the remaining 5.2 m of the Schattwald Beds according to this study. They are characterised by dark grey and black alterations of marl and thin bedded limestone and contain some siliciclastics (McRoberts et al., 1997). Bivalves and ammonites of Hettangian age occur in this interval. The palaeoenvironments of the Upper Schattwald Beds are interpreted to be shallow subtidal marine, due to the return of marine invertebrates, and salinity-controlled, due to the occurrence of brackish bivalve taxa (McRoberts et al., 1997). Reworked Rhaetian pebbles and desiccation cracks also indicate that the environment had to be intertidal or supratidal during some periods.

3.2.3 Lorüns oolite

The Lorüns oolite is a Hettangian unit (Furrer, 1993), which has a thickness of 25.5 m (this study) in the Lorüns quarry. Its lower boundary is taken as the first ooid-bearing carbonate above the Schattwald Beds, and the lithology is characterised by massively bedded, dark to light grey oolitic to oncolitic packstone and grainstone (McRoberts et al., 1997). My thin section analysis shows that the lower part of the formation is dominated by oolite packstone or packstone/ grainstone. The lithology shifts towards oncoidal/ oncolite packstone and oolite grainstone/packstone, which is more grainstone-dominated in the lower part of the formation. As my results show, the ooidal/ oncoidal packstone reappears in the uppermost part of the Lorüns oolite. The ooids have a diameter of up to 1 mm and the oncoids have a diameter of 1-10 mm in the Lorüns oolite (McRoberts et al., 1997). McRoberts et al. (1997) interpreted the Lorüns oolite to represent a broad barrier or bar in a shallow subtidal setting. Deposition likely occurred in the shallow-water lagoon or platform edge, due to the occurrence of stenotopic invertebrates indicative of marine salinities.

3.2.4 Hierlatz Limestone

The Hierlatz Limestone overlays the Lorüns oolite and consists of thick-bedded almost massive echinodermlimestones of red, grey, and white colour (Tollmann, 1976). The limestone contains crionoid detritus, with varying amounts of calcilutite matrix and is sometimes silicified. At the Lorüns quarry, the Hierlatz Limestone has a thickness of 13 m (this study). It was likely deposited during the late Hettangian, because of its stratigraphic position between the Hettangian Lorüns oolite and the Sinemurian Adnet Formation (Furrer, 1993). The occurrence of the Hierlatz Limestone has been related to active fracture zones (neptunian dykes) observed in the Lorüns oolite. Jenkyns (1971) interpreted the formation as reworked biogenic sands on submarine bars.

3.2.5 Adnet Formation

The Adnet Formation is a Sinemurian formation overlying the Hierlatz Limestone in Lorüns (Furrer, 1993). It consists of thin-bedded to intermediate-bedded red nodular limestone occurring with marls. At Lorüns the Adnet Formation has a thickness of 32 m. Three samples were taken from this lithology, but not analysed with thin sections. Hence, no further emphasis will be put on this formation.



Fig. 8. Stratigraphic overview of the sampled interval of Lorüns section in the Lorüns quarry near Bludenz, Austria, with indicated systems tracts. Highstand systems tract (HST), falling-stage systems tract (FSST), early transgressive systems tract (ETST) and late transgressive systems tract (LTST). Note that the colours used for the different units are not aimed to represent the reality, but rather for distinguishing between the different units.

4 Methods

4.1 Field procedure

The Lorüns section was measured and described in the Lorüns quarry, Austria by my supervisor Sylvain Richoz (*Fig.* 7). He sampled 71 whole-rock samples. Samples 1-20 were taken from the Kössen Formation, samples 21-51 from the Schattwald Beds, samples 52-66 from the Lorüns oolite, samples 67-68 from the Hierlatz Limestone and samples 69-71 from the Adnet Formation. The samples were then transported to Lund

University, Sweden, and were prepared and analysed by me.

4.2 Preparation of thin sections

According to macroscale observations and stratigraphic positions of the samples I picked out 36 samples for thin-section analysis: Lo5, 8, 11, 14, 17, 19, 23a, 23b, 25, 29, 33, 34, 39, 40, 41, 44, 46 and 50-68. The samples were cut using a Struers Discoplan-TS saw. I picked out one of the two slabs and polished it for 5-10 minutes in a Struers RotoPol-25 with a 600 grit diamond plate, until the surface of the rock was smooth. The rock was then cut once again to fit the size of the thin section glass (28X48 mm).

I wrote the name and the stratigraphic direction on the glass slides for the thin sections with a micro driller and then cleaned the slides using disinfectant. The glass slides were then grinded with a Struers Discoplan-TS and afterwards cleaned with ethanol. Cleaning with ethanol was also performed on the rock samples. I glued the slabs on the glass slides using epoxy proportions 15:2 between Struers' Epofix Resin and Epofix Hardener.

After drying the thin sections for two days, I removed excess epoxy from the thin sections with a razor blade and cut the glued slabs, so they reached a thickness of 1 mm. To make the rock components visible in the optical microscope, I polished the thin sections at 180 RPM using a grit size of 600. I finished the thin sections by polishing with a 1200-grit diamond plate.

4.3 Optical petrographic microscope

After preparing the thin sections I analysed all samples petrographically under the optical petrographic microscope, at the Department of Geology in Lund. The microscope used was an Olympus BX53F2 optical petrographic microscope. It had a camera and the possibility to display the sample in plane-polarised light (PPL) and crossed-polarised light (XPL). I used PPL for the petrographic analysis and XPL for distinguishing extinction patterns like echinoderm extinction or mineralogy. I used magnifications of 2X, 4X, 10X and 20X to analyse the samples at different scales.

The lithology of the sample was classified using the Dunham classification (Dunham, 1962) and microfacies were determined using the Standard Microfacies Types (SMF) (Wilson, 1975, modified by Flügel (2010)) (Fig. 9). For more grain-rich rocks than mudstones I analysed sorting, roundness, and percentage of grains. The degree of sorting was assessed using the classification of Tucker (1981); poorly sorted, moderately sorted, well sorted, and very well sorted. I analysed roundness by using the roundness scale for calcareous shell material from Pilkey et al. (1967). In this scale, the roundness of grains is divided into four categories where 1 is the least rounded and 4 the most rounded. I assessed the percentage of grains by estimating how much of the sample that is covered with coated grains or bioclasts in relation to matrix or cement. When applicable I also analysed the cement fabric in the Lorüns oolite.

4.4 LA-ICP-MS

4.4.1 Preparation of LA-ICP-MS analysis

I picked six thin sections for LA-ICP-MS analysis. These were Lo23a, Lo53, Lo54, Lo60, Lo64 and Lo66. These thin sections were scanned and printed in A3 sheet to better decide 5-11 spots in the sample for

- SMF 1: Spiculitic wackestone or packstone, often with calcisiltite matrix. Subtype emphasizes burrowing.
- SMF 2: Microbioclastic peloidal calcisilitie with fine grainstone and packstone fabrics.
- SMF 3: Pelagic lime mudstone and wackestones with abundant pelagic microfossils. Subtypes differentiate the groups of planktonic organisms.
- SMF 4: Microbreccia, bio- and lithoclastic packstone or rudstone.
- SMF 5: Allochthonous bioclastic grainstone, rudstone, packstone, floatstone, breccia with reef-derived biota.
- SMF 6: Densely packed reef rudstone.
- SMF 7: Organic boundstone. Subtypes try to differentiate the kind of contribution by potential reefbuilders to the formation of reefs and other buildups.
- SMF 8: Wackestones and floatstones with whole fossils and well-preserved endo- and epibiota.
- SMF 9: Strongly burrowed bioclastic wackestone.
- **SMF 10**: Bioclastic packstone and wackestone with abraded and worn skeletal grains.
- SMF 11: Coated bioclastic grainstone.
- SMF 12: Limestone with shell concentrations. Subtypes characterize shell-providing fossils.
- SMF 13: Oncoid rudstone and grainstone.
- SMF 14: Lag deposit.
- SMF 15: Oolite, commonly grainstone but also wackestone. Subtypes highlight the structure of ooids.
- SMF 16: Peloid grainstone and packstone. Subtypes differentiate non-laminated and laminated rocks.
- SMF 17: Grainstone with aggregate grains (grapestones).
- SMF 18: Bioclastic grainstone and packstone with abundant and rock-building benthic foraminifera or calcareous green algae. Subtypes describe the systematic assignment of the various groups.
- SMF 19: Densely laminated bindstone.
- SMF 20: Laminated stromatolitic bindstone/boundstone.
- SMF 21: Fenestral packstone and bindstone. Subtypes characterize fenestral voids and the contribution of calcimicrobes.
- SMF 22: Oncoid floatstone and wackestone.
- SMF 23: Non-laminated homogenous micrite or microsparite without fossils.
- SMF 24: Lithoclastic floatstone, rudstone or breccia.
- SMF 25: Laminated evaporite-carbonate mudstone.
- SMF 26: Pisoid cementstone, rudstone or packstone.

Fig. 9. Descriptions of the Standard Microfacies Types (SMF) from Wilson (1975) with modification from Flügel (2010).

LA-ICP-MS analysis. I picked the spots based on different categories: nuclei and cortices from ooids, oncoids and cortoids, matrix, cement, and bioclasts, which I divided into bivalves and echinoderms. For Lo23a and Lo53 I picked five spots each, for Lo54 and Lo64 I picked ten spots each, and for Lo60 and Lo66 I picked eleven spots each. These were marked on the A3 sheet. At the LA-ICP-MS I located the spots with a Live Camera and determined angle and location of the spots in detail. Laser spot size was set to 45x95 μ m, except for Lo54_2 where it was set to 39x110 μ m (same area) to better fit the analysed domain. Appendix 1 shows the location of all the spots photographed in the Live-Cam.

4.4.2 LA-ICP-MS analysis

Trace element analyses were done at the Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) laboratory at the Department of Geology, Lund University, using a Teledyne Photon Machines G2 laser, with a HelEx 2-volume sample cell, coupled to a Bruker Aurora Elite quadrupole ICP-MS.

Instrument tuning was done using SRM NIST612, aimed at stable signal counts on relevant isotopes, on low oxide production (below 0.5 % monitoring ²³⁸U/²³⁸U¹⁶O and ²³²Th/²³²Th¹⁶O) and on ²³²Th/²³⁸U ratios close to 1 (within 90 %). Certified SRM NIST612 reference glass was used as primary standard materials and SRM NIST614 and MACS3 was analysed as secondary quality check (Jochum et al. 2005; Jochum et al., 2011).

The isotopes analysed with LA-ICP-MS analysis were ⁴³Ca, ²⁶Mg, ⁸⁸Sr, ³¹P, ¹³⁷Ba, ⁶⁶Zn, ⁶⁵Cu, ⁵⁵Mn, ²³⁸U, ⁵¹V, ⁹⁸Mo, ¹⁸⁵Re, ⁷Li, ⁴⁹Ti, ²⁷Al, ²⁹Si, ⁸⁹Y and a selection of REE (¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁶³Dy, ¹⁶⁶Er, ¹⁷²Yb, ¹⁷⁵Lu). ⁶⁵Cu values were not further analysed after measurements due to interference with the LA-ICP-MS instrument.

Analytical session was setup to run automatically with standard-sample-standard bracketing, with roughly 10 unknowns between each standard block. Ablation was performed with a fluence of 2 J/cm² on carbonate and 3 J/cm² on the NIST glass and the laser repetition rate was set to 8 Hz with 240 shots per analyses. Baseline compositions were measured for 30 seconds before each measurement and subtraction was done with a step-forward approach.

4.4.3 Processing and evaluation of LA-ICP-MS data

I processed the data in the *Iolite* software (Paton et al., 2011), by removing outliers and by only selecting data from the time when the spots were made. In the software an internal standard calcium concentration of 40 wt% was set. This data was then imported to *Microsoft Excel* for evaluation. Mg, Mn and Sr might replace Ca in the crystal lattice due to the same charge (2+), and Al and Si can be bound to O to make silicates. To account for these elements the following formulas were applied for recalculating the Ca wt%:

$$Ca wt\%_n = \frac{Ca wt\%_o \cdot 100}{wt\%_n (Carbonate + oxides)}$$

Where $wt\%_n$ (*Carbonate* + oxides), is the recalculated percentage of carbonate and oxides, $Ca wt\%_o$ is the old Ca wt% (40 % as used in *Iolite*), $Ca wt\%_n$ is the new (true) Ca wt%, u is the atomic weight of the element or compound and ppm is the initially measured concentration of the elements in parts per million (ppm).

The new concentrations in ppm for the elements apart from Ca are calculated by the formula:

$$ppm_n = ppm_o \cdot \left(\frac{Ca \ wt\%_n}{Ca \ wt\%_o}\right)$$

Where ppm_n is the new concentration of the elements other than Ca and ppm_n is the old concentration of the elements other than Ca, measured with LA-ICP-MS.

For analysing the REE + Y concentrations, I normalised the values of these elements to the Post Archean Australian Average Shale (PAAS), developed by Taylor & McLennan, 1985. These values are based on the average REE/Y-concentrations of 23 post-Archean shales from Australia, which are thought to parallel the REE/Y-concentrations of the average upper continental crust (Taylor & McLennan, 1985). The PAAS values are for example shown in Table 2 in Chapter 7 from McLennan (1989). The formula for the recalculation is:

$$ppm_{nPAAS} = \frac{ppm_n}{PAAS \ value}$$

Where ppm_{nPAAS} is the new concentration of REEs and Y after PAAS normalisation and the *PAAS value* is

$$wt\%_{n}(Carbonate + oxides) = Ca wt\%_{o} \cdot \frac{100}{40} + \frac{Mg(ppm) \cdot \frac{uMgCO_{3}}{uMg} + Mn(ppm) \cdot \frac{uMnCO_{3}}{uMn} + Al(ppm) \cdot \frac{uAl_{2}O_{3}}{uAl} + Sr(ppm) \cdot \frac{uSrCO_{3}}{uSr} + Si(ppm) \cdot \frac{uSiO_{2}}{uSi}}{10000})$$

the concentration value of REEs and Y based on the average 23 post-Archean shales from Australia described above.

Ce is a REE with different redox states. In oxygenated water Ce^{3+} is oxidised to Ce^{4+} (Sholkovitz & Shen, 1995), which means that a negative or positive Ce anomaly has implications for the redox conditions in marine settings. A negative Ce anomaly indicates oxygenated seawater (de Baar et al. 1985; Elderfield & Greaves, 1982), while a positive Ce anomaly indicates local input of clastic material or anoxic conditions (de Baar et al., 1983; de Baar et al. 1988). I investigated this further by using the PAAS normalised REE values and applying the formula by Bau & Dulski (1996):

$$\frac{Pr_{PAAS}}{0.5Ce_{PAAS} + 0.5Nd_{PAAS}}$$

Where Pr_{PAAS} , Ce_{PAAS} and Nd_{PAAS} are the ppm_{nPAAS} for Pr, Ce and Nd. If the environment is oxygenated the ratio is >1, whereas in a more dysoxic environment the ratio is <1 (Bau & Dulski, 1996).

I also calculated the % Mg and % Ca in the samples by using the following formulas:

$$\%Mg = \frac{Mg \ wt\%_n}{u}$$
$$\%Ca = \frac{Ca \ wt\%_n}{u}$$

Where $Mg wt\%_n$ is the new Mg wt%, recalculated from $Ca wt\%_n$.

% Mg and % Ca can be used for calculating the mol % MgCO3:

$$mol \% MgCO_3 = \frac{Mg wt\%_n}{(Mg wt\%_n + Ca wt\%_n)}$$

I evaluated all spots, and the more important elements are described in detail in the results part. The main focus was on the coated grains, because these grains do not have a controlled mineralisation process like bivalves or echinoderms. I only calculated averages for the ooid and oncoid cortices because the cortices more directly record the in-situ environmental conditions, whereas the nuclei could have been transported considerable distances and consist of lithoclasts or quartz grains (Flügel, 2010).

4.5 Carbon isotope analysis

All of the 71 samples picked at Lorüns quarry were prepared for $\delta^{13}C_{carb}$ -analysis. I prepared all the samples at the Department of Geology, Lund. Samples that had not already been cut for thin sections were cut by a Struers Discoplan-TS. A Dremel 8100 driller was used to extract a fine powder from each of the samples, which was collected with paper and then filled into a testing tube. After finishing one sample the driller was disinfected in hydrochloric acid (HCl, 5 %) and distilled water. I made separate samples for oncoids, to compare the $\delta^{13}C_{carb}$ -signal from the oncoids with the matrix-signal. To better locate the oncoids I polished all samples containing oncoids. $\delta^{13}C_{carb}$ -measurements were not made before completing this thesis, so the results are not presented in this report.

5 Results

5.1 Petrographic descriptions and interpretations of samples from Lorüns

Below follows a description of all the analysed 36 thin sections. Every thin section is represented by at least one picture in Appendix 2.

Lo5 - SMF: 3. Lithology: Peloidal wackestone. Sorting: Moderately sorted. Roundness scale: 2. Percentage of grains: 20 %

The sample is a finegrained bioclastic, peloidal wackestone. The matrix is grey and contains sparite. Sparite indicates that significant recrystallisation occurred in the limestone after deposition. Bioclasts are rare and appear in shape of bivalve fragments, echinoderms and foraminifera. The sample has calcite veins, which can be related to the Alpine orogeny. I also observed a brown stylolite.

Lo8 – SMF: 3. Lithology: Peloidal wackestone. Sorting: Moderately sorted. Roundness scale: 2. Percentage of grains: 30 %

The sample is a peloidal wackestone containing bioclasts. The matrix is grey and contains more sparite than in Lo 5. Identified bioclasts are bivalve fragments, echinoderms, calcareous algae, foraminifera, and gastropods. The lower part of the sample is rich in clay minerals. Smaller calcite veins occur in the sample.

Lo11 – SMF: 10. Lithology: Packstone. Sorting: Poorly sorted. Roundness scale: 3. Percentage of grains: 60 %.

Packstone with diverse bioclast assemblage. It contains large bivalve fragments, gastropods, sponge spicules, and foraminifera. I also identified a bigger sponge in the sample. Peloidal intraclasts occur in the sample. The sample contains some stylolites and calcite veins.

Lo14 – SMF: 3. Lithology: Mudstone

Extremely fine-grained mudstone containing isolated bivalve fragments, echinoderms, sponge spicules, and foraminifera. The matrix is light grey with rare occurrence of sparite. The sample contains oxides and pyrite. Smaller calcite veins also occur in the sample.

Lo17 – SMF: 3. Lithology: Wackestone. Sorting: Poorly sorted. Roundness scale: 2. Percentage of grains: 20 %. Wackestone with sparse and isolated echinoderms, bivalve fragments, and sponge spicules. The sample contains oxides and pyrite. I observed some smaller calcite veins, and the micritic matrix is more coarse-grained compared to Lo14. Sparite occurs in the sample.

Lo19 – SMF: 10. Lithology: Wackestone. Sorting: Poorly sorted. Roundeness scale: 2. Percentage of grains: 50 %.

Wackestone, containing large amounts of bivalve fragments and sponge spicules. Bivalve fragments are of varying size and some of them are large. Other occurring bioclasts are echinoderms, calcareous algae, and gastropods. The bioclasts differ in colour between white, brownish, and grey. These colour differences might have developed because of different recrystallisation and dissolution processes. All bioclasts are surrounded by a grey, homogenous matrix. I observed several stylolites in the sample.

Lo23a – Lithology: Siltstone with lithoclasts of wackestone. For wackestone – SMF: 5. Roundness scale: 2. Percentage of grains: 30%.

The sample consists of a siltstone with two large lithoclasts of wackestone. The siltstone is mostly made up of quartz and contains smaller pieces of reworked carbonates, sparite, cortoids, echinoderms, and bivalve fragments. Two smaller, micritised coated grains occur, which are interpreted to be ooids. The sample is also stylolitised. The wackestone contains corals, bivalve fragments, echinoderms, sponge spicules, gastropods and foraminifera. The spatial relation between lithologies indicate that the depositional environment of the sample probably was a siliciclastic shore-environment, in which carbonates from the adjacent carbonate platforms were eroded into. Hence, this wackestone is allochthonous.

Lo23b – Lithology: Siltstone with allochthonous inclusions of carbonate lithoclasts.

Reddish oxidised siltstone containing quartz, clay minerals, and smaller carbonate lithoclasts. The carbonate parts of the rock were likely transported to the depositional environment of the siltstone.

Lo25 – Lithology: Siltstone with allochthonous inclusions of carbonate lithoclasts.

Reddish oxidised siltstone containing quartz and some smaller inclusions of carbonate lithoclasts. The sample shows interlayering between more quartzrich and darker, clay-rich intervals. Allochthonous carbonate lithoclasts appear small and rounded in the siltstone. The rock is devoid from fossils, except for a single echinoderm.

Lo29 – SMF: 3. Lithology: Mud/wackestone. Sorting: Poorly sorted. Roundness scale: 2. Percentage of grains: 10%.

The sample consists of a mud/wackestone with large amounts of micrite. The matrix is grey and uniform and contains isolated sparite. Bioclasts are rare and occur isolated. I identified bivalve fragments, echinoderms, foraminifera, and some other unclassified bioclasts. There seems to be some clay mineral input in the bottom of the sample and oxides occur as well. I also observed a small calcite vein in the sample.

Lo33 – SMF: 23. Lithology: Mudstone

Mudstone consisting of light-grey uniform micrite. I observed very few bivalve fragments, echinoderms, and sponge spicules. The sample also contains some stylolites.

Lo34 - SMF: 23. Lithology: Mudstone

Mudstone consisting of light-grey uniform micrite, very similar to Lo33. Bioclasts are very rare and difficult to classify. The sample contains several stylolites of different size.

Lo39 – SMF: 10. Lithology: Wackestone. Sorting: Moderately sorted. Roundness scale: 3. Percentage of grains: 20 %.

Wackestone with some clay mineral input. The matrix is grey and contains sparite. Bioclasts are spread out in the sample and appear as bivalve fragments, echinoderms, and calcareous algae. The sample contains minor amounts of quartz crystals.

Lo40 – SMF: 23. Lithology: Mudstone

The sample is a mudstone consisting almost entirely of micrite. It might be recrystallised due to the occurrence of sparite. Clay mineral input occurs in one part of the sample and the sample also contains a large calcite vein. Smaller calcite veins occur sporadically.

Lo41 – SMF: 10. Lithology: Bivalve packstone with lithoclasts of mudstone. For packstone – Sorting: Poorly sorted. Roundness scale: 3. Percentage of grains: 60 %.

Bivalve packstone containing two lithoclasts of mudstone. All bioclasts are bivalve fragments, except some echinoderms and foraminifera. Large amounts of the sample are made up of peloidal intraclasts. The mudstone lithoclasts are almost completely devoid of bioclasts and contain several calcite veins, which sometimes extend into the packstone.

Lo44 – SMF: 10. Lithology: Bivalve packstone and wackestone. For packstone – Sorting: Poorly sorted. Roundness scale: 3. Percentage of grains: 70 %. For wackestone – Sorting: Poorly sorted. Roundness scale: 2. Percentage of grains: 20%.

The sample consists of a bivalve packstone in the bottom which changes to a wackestone in the top. The packstone consists mostly of bivalve fragments of different sizes and alteration stages and peloidal intraclasts. A large calcite vein is also present in the packstone. The wackestone contains a more diverse assemblage of bioclasts in shape of bivalve fragments, echinoderms, and sponge spicules. There are several calcite veins in the wackestone. Clay minerals also occur in parts of the wackestone.

Lo46 – SMF: 10. Lithology: Wackestone. Sorting: Moderately sorted. Roundness scale: 3. Percentage of grains: 20 %.

Wackestone with abundant sparite. Echinoderms are the only identified bioclast. I also observed some quartz grains in the sample, indicating detrital input. The sample contains oxides.

Lo50 – SMF: 10. Lithology: Packstone. Sorting: Poorly sorted. Roundness scale: 3. Percentage of grains: 50 %.

Packstone containing many bioclasts. Identified bioclasts are small and large bivalve fragments, echinoderms, gastropods, sponge spicules, and foraminifera. Peloidal intraclasts are common in the sample. The sample contains several stylolites and has some major sparite cements as well. I also observed minor amounts of quartz in the sample.

Lo51 – SMF: 10. Lithology: Wackestone. Sorting: Poorly sorted. Roundness scale: 2. Percentage of grains: 40 %.

Wackestone with clay mineral input. Identified bioclasts are bivalve fragments, echinoderms, gastropods, calcareous algae, and sponge spicules. Most of these are rather small and are spread out over the whole sample. Peloidal intraclasts occur in the sample but are not very common. Large parts of the sample are covered by clay minerals, indicating terrestrial influx to the carbonate platform. The occurrence of quartz in the sample strengthens this interpretation. I also observed marcasite and pyrite in the sample.

Lo52 – SMF: 10. Lithology: Packstone. Sorting: Poorly sorted. Roundness scale: 3. Percentage of grains: 70 %.

Bioclast-rich packstone containing some large bioclasts. The identified bioclasts are bivalve fragments, echinoderms, and gastropods. Peloidal intraclasts are very common in the sample. A large vein of calcite with a stylolite runs diagonally through this sample. This vein is interpreted to be a late diagenetic fill, likely related to the Alpine orogeny. The whole sample is also cut through by several other calcite veins.

Lo53 – SMF: 10. Lithology. Coated bioclastic packstone. Sorting: Poorly sorted. Roundness scale: 4. Percentage of grains: 50 %.

The sample consists of a coated bioclastic packstone with many bioclasts and some coated grains and is almost completely dolomitised. The dolomite crystals show little intercrystalline porosity. Bivalve fragments, echinoderms, calcareous algae, sponge spicules, and gastropods occur in the sample. The bivalve fragments are less prominent and smaller in this sample as compared to Lo52. Many bioclasts and grains show a micritic coating. Most of them I interpret as cortoids but ooids also occur occasionally. The ooids appear with a yellow dolomitised nucleus and cortex and have a thick micritised rim around them. The sample also contains several calcite veins.

Lo54 – SMF: 15M. Lithology: Oolite packstone. Sorting: Moderately sorted. Roundness scale: 4. Percentage of grains: 80 %.

The sample is an oolite packstone, occasionally containing bioclasts. The ooids are micritised and some of them are clearly laminated. Ooids sometimes form polyooids. Cortoids and oncoids are rarer in the sample. Present bioclasts are bivalve fragments, echinoderms, calcareous algae, and gastropods. The sample also contains stylolites and larger and smaller calcite veins.

Lo55 – SMF: 15M. Lithology: Oolite grainstone/ packstone. Sorting: Moderately sorted. Roundness scale: 4. Percentage of grains: 80 %. Cement fabric: Blocky.

Oolite grainstone/packstone, showing a variety of different coated grains. This sample contains more cement than Lo54, but some areas are covered with a lime mud matrix. Ooids are prominent and are laminated and micritised. Sometimes they form polyooids. Several grains I interpret as cortoids because they show direct micritisation around bioclasts and few grains are oncoids. Bioclasts appearing in the sample are bivalve fragments, echinoderms, and gastropods. Some parts of the sample are weakly dolomitised. The sample contains a stylolite, a major calcite vein, and some smaller calcite veins.

Lo56 – SMF: 11. Lithology: Cortoid packstone with oncoids. Sorting: Poorly sorted. Roundness scale: 4. Percentage of grains: 80 %.

The sample is a cortoid packstone, containing cortoids and oncoids. Ooids are absent. Most of the sample contains a micritic matrix, but cement appears occasionally. Lo56 is also less sorted compared with the previous samples, showing a greater amount of major coated grains surrounded by much smaller coated grains. The main bioclasts in this sample are echinoderms and bivalve fragments. Foraminifera and gastropods also occur occasionally. As in Lo55 some parts of the sample are dolomitised. Calcite veins and precipitates are common in the sample, and there is also a stylolite in the sample.

Lo57 – SMF: 22. Lithology: Oncoidal packstone with cortoids. Sorting: Moderately sorted. Roundness scale: 4. Percentage of grains: 40 %.

Oncoidal packstone, containing oncoids, cortoids, and abundant bioclasts. Matrix dominates dominates over cement in all except one part of the sample. The oncoids are of varying size and some of them are very large. Cortoids are smaller and show clear micritisation rims. Ooids are absent from the sample. Identified bioclasts are bivalve fragments and echinoderms which are spread over the entire sample. Calcareous algae occur too but are less frequent. A major calcite vein runs diagonally through the sample and shows intertwining with stylolites. This might indicate that calcite during the Alpine orogeny was precipitated preferentially in zones of weaknesses in the rock, e.g., stylolites.

Lo58 – SMF: 22. Lithology: Cortoid packstone with oncoids. Sorting: Poorly sorted. Roundness scale: 4. Percentage of grains: 40 %.

Cortoid packstone, containing cortoids and oncoids with a dominance of cortoids. Ooids are absent. Bioclasts include bivalve fragments, echinoderms, calcareous algae, and gastropods. Some parts of the sample are slightly dolomitised. The sample contains many calcite veins and a stylolite. Lo59 – SMF: 22. Lithology: Oncoidal packstone. Sorting: Poorly sorted. Roundness scale: 4. Percentage of grains: 40 %.

The sample is an oncoidal packstone, containing oncoids, cortoids, and bioclasts. Oncoids and cortoids are similar to Lo57 and Lo58 and bivalve fragments, echinoderms and gastropods occur in abundance over the whole sample. Ooids are absent in the sample. Large parts of the sample are dolomitised. Calcite veins occur in the whole sample, and I observed a major stylolite in the upper part of the sample.

Lo60 – SMF: 13. Lithology: Oncolite packstone. Sorting: Poorly sorted. Roundness scale: 4. Percentage of grains: 70 %.

Oncolite packstone, containing oncoids and cortoids. The oncoids are well-laminated and can reach considerable sizes. Cortoids are common and occur in most of the sample, while ooids are absent. Bioclasts are less common than in Lo59 and appear in shape of bivalve fragments and echinoderms. Some parts of the sample are dolomitised. The sample is stylolitised. Calcite veins occur but are less prominent than in Lo59.

Lo61 – SMF: 15M. Lithology: Oolite grainstone/ packstone. Sorting: Well sorted. Roundness scale: 4. Percentage of grains: 80 %. Cement fabric: Blocky.

Oolite grainstone/packstone, mostly made up of ooids and some other coated grains. The sample contains more cement than matrix. All ooids are micritised and occasionally occur as polyooids. Cortoids and oncoids also occur in this sample but are less common than ooids. Identified bioclasts are bivalve fragments, echinoderms, and calcareous algae. Some of these bioclasts are large but they occur rarely in the sample. The sample contains calcite veins and is also stylolitised.

Lo62 – SMF: 15M. Lithology: Oolite packstone. Sorting: Well sorted. Roundness scale: 4. Percentage of grains: 80 %.

Oolite packstone, consisting mostly of ooids as Lo61. Micritic matrix dominates over cement in this sample, although cement is prominent in some areas. The ooids are micritised, sometimes laminated, closely packed and occasionally form polyooids. Less common in this sample are cortoids and oncoids. Bivalve fragments, echinoderms, and gastropods occur in the sample. The sample contains calcite veins and stylolites.

Lo63 – SMF: 15M. Oolite grainstone. Sorting: Well sorted. Roundness scale: 4. Percentage of grains: 80 %. Cement fabric: Blocky. Some grains also have isopachous cements around them.

The sample is an oolite grainstone, containing ooids and cortoids. Cement completely dominates over matrix, which is nearly absent in this sample. The ooids are often weakly micritised but lack a clear lamination. In the sample they sometimes form polyooids. Oncoids also occur but are rarer. Identified bioclasts are bivalve fragments, echinoderms, calcareous algae, and foraminifera. Some calcareous algae occur in a tight colony in this sample. The sample contains calcite veins and is stylolitised.

Lo64 – SMF: 15M. Lithology: Oolite grainstone/ packstone. Sorting: Well sorted. Roundness scale: 4. Percentage of grains: 80 %. Cement fabric: Blocky.

Oolite grainstone/packstone, consisting mostly of well-sorted ooids. Cement is more abundant than matrix, but the matrix is dominant in some parts of the sample. The ooids are micritised and sometimes laminated. Some ooids are recrystallized in the sample and some appear as polyooids. Oncoids and cortoids also occur but are not as common as ooids. Bioclasts are almost completely absent except some bivalve fragments and echinoderms. Calcite veins are spread out over the sample. One of the calcite veins is also associated with a stylolite.

Lo65 – SMF: 22. Lithology: Oncolite packstone. Sorting: Poorly sorted. Roundness scale: 4. Percentage of grains: 80 %.

Oncolite packstone, containing oncoids and other coated grains. The oncoids are prominent in this sample and can reach large sizes. Cortoids are also common, while ooids are less frequent and are micritised and laminated. Identified bioclasts are bivalve fragments, echinoderms, calcareous algae, gastropods, and foraminifera. The sample contains several calcite veins, which are sometimes associated with stylolites.

Lo66 – SMF: 15M. Lithology: Oolitic packstone. Sorting: Poorly sorted. Roundness scale: 4. Percentage of grains: 70 %.

Oolitic packstone, consisting of mostly ooids and matrix. The ooids are micritised and laminated. Some of them are recrystallised. Other coated grains are oncoids and cortoids but they are less common than ooids in this sample. The sample contains a neptunian dyke from the overlying Hierlatz Limestone. Bioclasts appear in the shape of bivalve fragments, echinoderms, gastropods, and foraminifera. The sample contains one major calcite vein and several smaller calcite veins.

Lo67 – SMF: 10. Lithology: Echinoderm packstone. Sorting: Well sorted. Roundness scale: 3. Percentage of grains: 60 %.

Echinoderm packstone, consisting mainly of echinoderms embedded in a muddy matrix. Echinoderms appear in different sizes and shapes and are prominently represented by crinoids. Bivalve fragments, gastropods, and foraminifera are also very common in the sample. The sample contains two intraclasts and some intervals with less frequently occurring fossils. Calcite veins and are common in the sample. Several stylolites occur and one of them is associated with parts of the outer rim of one intraclast. This intraclast is large and mostly composed of a greyish matrix. It contains mostly small bioclasts of different alteration stages.

Lo68 – SMF: 10. Lithology: Wackestone. Sorting: Moderately sorted. Roundness scale: 2. Percentage of grains: 20 %.

Wackestone, mostly consisting of micrite ma-

trix, small bioclasts, and sparite. Identified bioclasts of this sample are bivalve fragments, echinoderms, sponge spicules, and foraminifera. The sample contains several calcite veins and is also stylolitised.

5.2 Summary of petrography from samples from Lorüns

To summarise, the analysed part of the Kössen Formation consists mostly of wackestone or packstone, containing peloids, sparite, and a diverse fossil assemblage. Common fossils are bivalve fragments, echinoderms, calcareous algae, foraminifera, gastropods, and sponge spicules.

At the base of the Schattwald Beds (Lo23a), the lithology shifts towards siltstone which in some samples contains lithoclasts of Kössen type carbonates. The lowest part of the Schattwald Beds is quartz-rich, contains clay minerals and is very colourful. Two micritised ooids occur in the lower part of the Lower Schattwald Beds (Lo23a) (Fig. 10a). At Lo29, I observed a shift towards mud/wackestone. Due to this shift in lithology, I put the boundary between the Lower and Upper Schattwald Beds at Lo29. The fossil content of Lo29 consists of few and isolated bivalve fragments, echinoderms, and foraminifera and the number of fossils decreases even more in the following thin sections. In the upper part of the Schattwald Beds (Lo41) lithology shifts towards a fossiliferous packstone, marking the end of the fossil-poor lithologies from the Lower Schattwald Beds to Lo41, and the end of the "Extinction interval" (*Fig.* 11b). Clay minerals and quartz appear in several samples of the Upper Schattwald Beds and indicate a proximal setting for Lorüns during this time.

The Lorüns oolite consists mostly of coated grains and shows alternation between more ooiddominated grainstone/packstone and more oncoiddominated packstone. All ooids in the formation are micritised but some still show laminations (Fig. 10b). However, it is always impossible to see if the original position of the ooid crystal was radial or concentric. In several samples some of the ooids occur lumped together as polyooids. Other coated grains in the formation are oncoids (Fig. 10c) and cortoids (Fig. 10d), which vary in abundance in the samples. Bioclasts in shape of bivalve fragments, echinoderms, calcareous algae, gastropods, and foraminifera appear in many of the samples but are more rare than coated grains. The top of the Lorüns oolite (Lo66) is marked by a neptunian dyke from the Hierlatz Limestone.

The Hierlatz Limestone marks the return of bioclast-dominated samples. Crinoid plates are especially prominent, but many other fossils occur as well. In the upper part of the formation the amount of bioclasts declines and the lithology goes from packstone to wackestone.

Stylolites and calcite veins are common in all analysed formations. These features are related to the Alpine orogeny. Some of the samples in the Kössen Formation and the Schattwald Beds also contain oxides, pyrite, or marcasite.





b)

*Fig.*10. Coated grain selection from the Lorüns section. a) Micritised ooid from the Lower Schattwald Beds (Lo23a). b) Micritised ooid with laminations from the Lorüns oolite (Lo54). c) Big oncoid from the Lorüns oolite (Lo59). d) Cortoid from the Lorüns oolite (Lo60).

5.3 Logs of the lithologic units at Lorüns

Fig. 11 shows stratigraphic logs of the Kössen Formation (a), the Schattwald Beds (b), and the Lorüns oolite (c). The stratigraphy is based on petrographic observations from thin sections and in the field. The T-Bed marks a bed with increasing clay content and thin laminations, which is terminated by a black and bituminous top layer (Hillebrandt et al., 2013). In Lorüns, the T-Bed is represented by the Lower Schattwald

Beds, and the bituminous top layer is present as a 2-cm shale bed in the uppermost part of the Lower Schattwald Beds. This shale bed also represents the peak of the ETE and is termed the "ETE-peak". As can be seen in Fig. 11c, the base of the Lorüns oolite is set at Lo52, which has a Schattwald Bed lithology. The reason for this is that Lo52 in the field belonged to the massive unit of the Lorüns oolite and therefore was put into this unit, although it has a different lithology. Note also, the indicated neptunian dyke in Lo66 and the lithological shift to the Hierlatz Limestone at Lo67.

Height (m)





b)

28



Legend



Fig. 11. Stratigraphic logs of the Zirmenkopf Member of the Kössen Formation (a), the Schattwald Beds (b) and the Lorüns oolite and the lowermost part of the Hierlatz Limestone (Lo67) (c). Lo68 was sampled 1.9 m above Lo67. The legend for the logs is shown in *Fig.* 8d. The Dunham classification scale shown in *Fig.* 8d consists of mudstone (m), wackestone (w), packstone (p), grainstone (g), floatstone (f), rudstone (r) and boundstone (b).

5.4 Sequence stratigraphy

Sequence stratigraphy has been interpreted for the analysed formations and is indicated in Fig. 8. The Kössen Formation at Lorüns is characterised by limestones with a high fossil diversity. This observation is consistent with marine conditions during deposition. Therefore, the Kössen Formation is interpreted to represent a highstand systems tract (HST). At the base of the Lower Schattwald Beds, there is an abrupt shift towards siliciclastic deposition, likely linked to a regression. This shift might be linked to the development of a falling-stage systems tract (FSST), but because of the proximal setting of Lorüns, it is not clear if this still is a HST. The shift between the Lower and Upper Schattwald Beds is marked by a return to carbonate deposition, connected to a transgression. Due to the common occurrence of clay minerals and quartz, the Upper Schattwald Beds might represent an early transgressive systems tract (ETST). I interpreted the transgression to continue throughout the Upper Schattwald Beds and the Lorüns oolite, where coated grains are deposited in a shallow marine environment. The Hierlatz Limestone, with its high crinoid abundance, and the Adnet Formation, which consists of condensed nodular limestone (type ammonitico rosso), are also linked to the transgression. Therefore, the strata from Upper Schattwald Beds until the Adnet Formation are interpreted to be the transgressive systems tract (TST).

5.5. LA-ICP-MS

5.5.1 Average major and trace-elemental concentrations

Fig. 12 shows the average values in ppm of the major and trace elements analysed with LA-ICP-MS, divided into the categories nuclei, cortices, cements, matrices, bivalves, and echinoderms. The values for the nuclei and cortices except for V and U follow each other closely. The cement, matrix, bivalves, and echinoderms are slightly different but display the same overall trends. Note that the highest values in general are recorded in elements that substitute for Ca in CaCO₃ or elements that bind with O₂ to form silicates, like Mg, Al or Si. The bivalve graph is discontinuous because Al, Si, Ti, and Re were not detected. Note that Re was detected in minimal amounts (<0.01 ppm) only in three nucleus or cortex samples (Lo53_1, Lo53_2, Lo60_3).

5.5.2 Mineralogy of carbonate grains

I analysed the original mineralogy of the carbonate grains by calculating the mol % MgCO₃ and by analysing the Sr values (ppm) in the samples. The mol % MgCO₃ in the different spots is shown in *Fig.* 13 for all spots (a) and only for coated grains (b). As can be seen in *Fig.* 13a, most spots have mol % <4, which



Fig. 12. Average elemental concentrations of major and trace elements analysed with LA-ICP-MS in Lorüns, divided into nuclei, cortices, cement, matrix, bivalves, and echinoderms.

indicates that they are composed of low-Mg calcite or aragonite. Six spots show a mol % >4, which implies high-Mg calcite. These spots are Lo53_2 (ooid cortex), Lo53_3 (echinoderm), Lo53_4 (matrix), Lo60_1 (oncoid nucleus), Lo60_4 (cortoid nucleus) and Lo60_11 (oncoid cortex). Most of the other spots show values < 2 mol % accounting for an overall average of 2.24 mol %.

Fig. 13b shows the mol % MgCO₃ in the nuclei and cortices of coated grains. Ooid cortices and nuclei are all <4 mol %, except for Lo53_2. Oncoid cortices show on average higher values than ooid cortices (3.29 mol % compared to 1.80 mol %), but also a higher standard deviation (3.22 compared to 1.15). One oncoid cortex has a mol % MgCO₃ > 4 (Lo 60_11). The two oncoid nuclei show completely different mol % (11.8 mol % and 1.54 mol %). Among the cortoids the nucleus has a mol % >4 (5.25 mol %).

The Sr values (ppm) in the different spots are shown in Fig. 14 for all spots (a) and only for coated grains (b). As can be seen in Fig. 14a all Sr values are low. There is a general trend from higher to lower Sr values the younger the strata get. The highest values (Sr > 500 ppm) are encountered in spots from the sample Lo23a from the Schattwald Beds, and samples Lo53 and Lo54 from the Lorüns oolite. The lowest Sr value is recorded in a cement from the Schattwald Beds (Lo23a 5) and is considerably lower than all other values (27.4 ppm). On average Sr-values are ~ 264 ppm. When comparing the Sr-values for the coated grains, all coated grains have very similar Srvalues, but the ooids generally show a higher variety than oncoids (ooid cortex average: 200 ± 81.2 ppm; oncoid cortex average: 211 ± 43 ppm) (*Fig.* 14b).

5.5.3 Weathering

Fig. 15a shows the values of Al (ppm), as an indicator of the clay minerals, and Si+Al (ppm) as a measure of the siliciclastics for all the analysed spots. Al values in the Schattwald Beds and the lower part of the Lorüns oolite vary without a specific trend and reach their highest value in an oncoid cortex (Lo60 10). In the upper part of the Lorüns oolite (Lo64 and Lo66) Al values decrease sharply. The terrestrial input from siliciclastics (Si+Al) is the most in the Schattwald Beds and varies without a specific trend in the lower part of the Lorüns oolite. As for the Al, Si+Al also decreases in the upper part of the Lorüns oolite (Lo64 and Lo66), where Si values are below detection limit in several spots. Higher Si+Al-values are recorded in some coated grains in the topmost sample of the Lorüns oolite (Lo66).

Fig 15b. shows the values of Ti (ppm) for all the analysed spots. Ti is in this case used as a proxy for the amount of weathering. As the figure shows, Ti has the highest values in the Schattwald Beds and the lower part of the Lorüns oolite (Lo53 and Lo54) and shows a decrease to the uppermost part of the Lorüns oolite. This means that the amount of weathering decreased after the deposition of the Lower Schattwald Beds at Lorüns.

The Al, Si, and Ti values in coated grains are shown in Appendix 3. The values generally decrease upsection for the cortices and nuclei for Al, the cortices for Si, while this trend is lacking in the ooid nuclei for Si and in the ooid nuclei and cortices for Ti. Interestingly, the cortex value from the ooid from the Schattwald Beds is significantly higher than the nucleus value for Al, Si and Ti. The oncoid cortices have much higher averages compared to the ooid cortices for Al and Si, but because of the very high error margins, I do not consider these differences to be of any significance.



b)

Fig. 13. Mol % MgCO₃ in the spots analysed with LA-ICP-MS in Lorüns. a) Mol % MgCO₃ for all the analysed spots. The sample from the Schattwald Beds is represented with a grey line and samples from the Lorüns oolite are represented with a yellow line. b) Mol % MgCO₃ for the spots from coated grains. The samples are presented for each coated grain in stratigraphic order from left to right. The threshold value for high-Mg calcite (4 mol %) is highlighted with a red stippled line and samples with dolomitisation are highlighted with a golden box in *Fig.* 13a and *Fig.* 13b.





Fig. 14. Sr (ppm) in the spots analysed with LA-ICP-MS in Lorüns. a) Sr (ppm) for all the analysed spots. The sample from the Schattwald Beds is represented with a grey line and samples from the Lorüns oolite are represented with a yellow line. b) Sr (ppm) for the spots from coated grains. The samples are presented for each coated grain in stratigraphic order from left to right.

5.5.4 Mn

The Mn values (ppm) in the different spots are shown in *Fig.* 16 for all spots (a) and only for coated grains (b). After correlations with Al, Sr and Ti, spots $Lo23a_2$ and $Lo23a_3$ are considered to be outliers with likely an influence of detrital origin and will not be considered in the evaluation of Mn (see section 6.3.2., *Fig.* 22a, b). As can be seen in Fig. 16a there is a general trend from higher to lower Mn-values the younger the strata get. The higher values in Lo23a_1 (nucleus) and in the lower part of the Lorüns oolite,



Fig. 15. Values of some detrital elements for the spots analysed with LA-ICP-MS in Lorüns. a) Al, which represents clay weathering compared to Si+Al, which represents siliciclastic weathering, for all the analysed spots. b) Ti, which is a general weathering indicator, for all the analysed spots. The sample from the Schattwald Beds is represented with a grey line and samples from the Lorüns oolite are represented with a yellow line.

indicate that slight dysoxic conditions might have persisted at Lorüns during the extinction interval in the Lower Schattwald Beds, and in the recovery period of the Lorüns oolite. Ooid cortices and nuclei also show a decrease of Mn values from the Schattwald Beds to the Lorüns oolite (*Fig.* 16b), which strengthens the interpretation of dysoxia at least in the sediments during and directly after the extinction.

5.5.5 REE + Y

Fig. 17a shows the average values after PAAS normalisation (Taylor & McLennan, 1985) of Rare Earth Elements (REEs) and Y analysed with LA-ICP-MS. Their distribution in the nuclei, cortices, cements, matrices, bivalves and echinoderms is shown in *Fig.* 17a. All categories display a very similar REE/Y pattern with a



Fig. 16. Mn (ppm) in the spots analysed with LA-ICP-MS in Lorüns. a) Mn (ppm) for all the analysed spots. The sample from the Schattwald Beds is represented with a grey line and samples from the Lorüns oolite are represented with a yellow line. b) Mn (ppm) for the spots from coated grains. The samples are presented for each coated grain in stratigraphic order from left to right.

negative Ce-anomaly and a positive Y-anomaly. The cement is enriched in all REE except Ce, when compared to the other categories. This enrichment is mostly due to the cement spot Lo23a_5, which shows considerably higher values than all other cements (*Fig.* 17a). A possible explanation for this could be that Lo23a_5 is the only cement taken from the siliclastic Lower Schattwald Beds, which might have another cement signature than the carbonate environment of the Lorüns oolite.

Fig. 17b shows the average values after PAAS normalisation of REE/Y for nuclei and cortices of the coated grains. All categories follow a similar pattern for the REE/Y with a negative Ce-anomaly and a positive Y-anomaly. The oncoid nuclei and cortices are very closely correlated, while the ooid nuclei and cortices are similar but not as related as the oncoid nuclei and cortices show higher values than the oncoid and cortoid nuclei and cortices. The REE/Y-plots in both *Fig.* 17a and b display a slight HREE-enrichment, which is consistent with the common REE-pattern in seawater (see "Background").

To better analyse the stratigraphic distribution of the REE/Y-distribution, I compared the REEcontent of the ooid cortex spot from the Schattwald Beds (Lo23a 2) with averaged values for ooid cortices and oncoid cortices from the Lorüns oolite. The resulting plots are shown in Fig. 18. As can be seen from the diagram, the ooid cortex from the Schattwald Beds has a much higher amount of REE/Y than the ooid and oncoid cortices from the Lorüns oolite. This explains the discrepancy in REE/Ys between the ooids and other coated grains in Fig. 17b. The negative Ce-anomaly is pronounced in the ooid cortex from the Schattwald Beds, while the positive Y-anomaly is absent. MREE enrichment also occurs in the ooid cortex from the Schattwald Beds. The ooid cortices and oncoid cortices from the Lorüns oolite follow each other closely, and show a negative Ce-anomaly, a positive Yanomaly, and HREE enrichment.

5.5.6 The Ce-anomaly

I analysed the Ce-anomaly by using the formula from Bau & Dulski (1996):

$$\frac{Pr_{PAAS}}{0.5Ce_{PAAs} + 0.5Nd_{PAAs}}$$

Fig. 19 shows the Ce-anomaly for all the spots after PAAS-normalisation and application of the formula above. All the spots except Lo66_6 and Lo66_7 have values >1, which means oxygenated conditions. Lo66_6 and Lo66_7 also have values very close to 1 (~0.99 and ~0.96 respectively). Hence, the Lorüns section was well oxygenated during most of the Rhaetian and Hettangian.

5.5.7 Other major elements and trace elements

Appendix 3 shows the amounts in ppm for the elements Li, Al, Si, P, Ti, V, Zn, Mo, Ba and U in coated grains from the Lorüns section. As can be seen from the figures and the calculated averages for ooid and oncoid cortices, no major differences of elemental amounts between the coated grains are recorded. The continuously low amounts of some elements, like U, in the coated grains also imply that it is difficult to assess palaeoenvironmental conditions based on these elements.

6 Discussion

6.1 Petrographic analyses and depositional setting

As described in the results part and the stratigraphic log, the Lorüns oolite dominantly consists of oolite grainstone/packstone or oncoidal packstone. Variations between the amount of cement and micrite can be ascribed to differences in water energy levels (Flügel, 2010). Carbonate cements are favoured by high water energy while micrite is preferentially formed in lower water energy. Deposition of the Lorüns oolite clearly occurred in the photic zone because of the occurrence of cortoids in all thin sections, and calcareous algae in many of the thin sections (Flügel, 2010). Ooids often appear as polyooids, which Flügel (2010) sees as an indicator for the upper euphotic zone. Due to the abundance of ooids, deposition of the Lorüns oolite likely occurred in warm, saline, shallow-marine environments in the tropics or lower subtropics, but not very near to the equator (cf. Flügel, 2010; Lees, 1975). This interpretation is also consistent with the geographic position of Lorüns in the NCA during the ETE-event (Lindström et al., 2021) (see Fig. 3).

Fig. 20a shows an idealised depositional model for a carbonate ramp containing coated grains (Esrafili -Dizaji & Rahimpour-Bonab, 2014), which can be applied to the carbonate platform at Lorüns. As can be seen from the figure the back-shoal is characterised by oncoid- and peloid bearing ooid grainstone and packstone, the fore-shoal is characterised by bioclastic, ooid grainstone and packstone, and the central shoal is characterised by cross-bedded, well-sorted oolitic grainstone (Esrafili-Dizaji & Rahimpour-Bonab, 2014). The lagoon is characterised by the occurrence of oncoids but no ooids. The lowermost part of the Lorüns oolite (Lo53-Lo55) consists of oolite grainstone/packstone, containing oncoids. According to the depositional model from Esrafili-Dizaji & Rahimpour-Bonab (2014), this part of the Lorüns oolite was deposited in the back-shoal, due to the co-occurrence of ooids and oncoids. Ooids are absent in the oncoidal packstone-dominated samples Lo56-Lo60. This means that deposition of this part of the Lorüns oolite occurred in the lagoon. Ooid grainstone/packstone with varying amounts of cement returns in Lo61 and is present upsection until the top of the Lorüns oolite. Because oncoids also are present in all of these samples, this lithological shift also indicates an environmental change towards the back-shoal in Lo61-Lo66.

Coated grains are lacking in the Kössen Formation, but I observed two micritised ooids in the


Fig. 17. Average elemental values of REE/Y analysed with LA-ICP-MS in Lorüns. a) Nuclei, cortices, cement, matrix, bivalves and echinoderms. b) Coated grains. (n): nuclei, (c) cortices.



Fig. 18. REE/Y-content in the ooid cortex from the Schattwald Beds (Ooid (c) S.B.), and averaged REE/Y-content in the ooid cortices from the Lorüns oolite (Ooid (c) Lorüns oolite) and in the oncoid cortices from the Lorüns oolite (Oncoid (c) Lorüns oolite). (n): nuclei, (c) cortices.



Fig. 19. Calculation of the Ce-anomaly with Nd for all spots analysed with LA-ICP-MS. If the values are >1 the conditions are oxygenated while values of <1 indicate a more dysoxic environment. The stippled red line highlights the threshold value of 1 for oxygenated waters.

Lower Schattwald Beds (Lo23a). I interpret the ooids in the Lower Schattwald Beds to be allochthonous because they occur in a siltstone, which was deposited in a siliciclastic shore environment unfavourable for coated grain formation. Due to the Kössen Formation association of the wackestone lithoclasts in Lo23a, it is likely that the ooids also might have originated in the Kössen Formation.

Throughout the whole Lorüns section a wide range of bioclast preservation is seen. For example, the bivalves in Lo23a and Lo44 either have a brown or white colour. This difference is likely due to the mineral replacement processes of the bivalves, where the white bivalves have been completely dissolved and precipitated, while the brown bivalves only have been slightly recrystallised. In the Lorüns oolite, dolomitisation is common in many of the samples. In these samples, dolomite crystals are concentrated in some parts of the sample, but usually do not completely dominate it. Therefore, I interpret the dolomitisation to have occurred during early diagenesis, rather than being precipitated directly from the seawater.



Fig. 20. Idealised depositional model of a carbonate ramp containing coated grains. The dominating coated grains in each environment are indicated in the figure. (Esrafili-Dizaji & Rahimpour-Bonab, 2014)

6.2 Sequence stratigraphy

The sequence stratigraphy and connected sea-level changes around the TJB have been reviewed by several authors. McRoberts et al. (1997) argue that the Kössen Formation and the Lower Schattwald Beds represent a HST and that the top of the Lower Schattwald Beds represents a sequence boundary (SB). The LST might be lacking in some places of the NCA, because the limestone at the top of the Kössen Formation is still part of the HST and its top might represent a sequence boundary (McRoberts et al. 2012). According to McRoberts et al. (1997), the Upper Schattwald Beds and Lorüns oolite represent a transgressive systems tract (TST), because these units are deepening upward. This makes McRoberts et al. (1997) propose a regression-transgression scenario at Lorüns. Tollmann (1976), Hallam (1981) and McRoberts (1994) have observed similar sea-level changes in the NCA and other localities in the western Tethys and northwest Europe. van de Schootbrugge et al. (2013) confirm the regression at the end of the Triassic, and transgression in the early Jurassic along the margins of the Tethys Ocean, but also argue that the sea-level rise is recorded in Panthalassa. The early Jurassic transgression might therefore have been global, with major tectonic overprints at the Tethyan margins.

The sequence stratigraphic interpretation of this study is in general agreement with that of McRoberts et al. (1997). The only difference is that I interpreted the Lower Schattwald Beds to possibly represent a FSST, because of its siliciclastic composition. McRoberts et al. (1997) argue for a sequence boundary (SB) on top of the Lower Schattwald Beds as conclusion for the HST. I agree that there might be a SB in shape of a transgressive surface (Flügel, 2010) on top of the Lower Schattwald Beds, as there is a distinct shift towards deeper-water facies in the Upper Schattwald Beds marked by a return of carbonate deposition. The transgression clearly starts at the onset of the Upper Schattwald Beds with the return of carbonate deposition and continues into the Lorüns oolite, which shows shallow marine conditions with coated grains and marine fossils. The Hierlatz Limestone and Adnet Limestone show deeper marine conditions (this study; Kindle, 1991). To put the ETST and LTST all the way from the Upper Schattwald Beds to the Adnet Formation is therefore a reasonable alternative.

6.3 The demise of the carbonate platform at Lorüns and the role of ocean acidification

Reduced biological carbonate production and the extinction of reef builders and reef dwellers as a consequence of the ETE likely led to the demise of rimmed platforms, like the Dachstein platform (Pálfy et al., 2021). Due to the earliest Hettangian transgression also bottom water energy regimes changed during this period. These factors led to a transition from a rimmed platform to an offshore carbonate ramp (Pálfy et al., 2021), where the ooid shoals described in section 6.1 formed a microbially cemented margin during the development of the Lorüns oolite.

As described in the "Background" ocean acidification is caused by the volcanogenic emissions of CO_2 and SO_2 from the CAMP. Kump et al. (2009)



Fig. 21. Flow chart showing possible cascading effects of CAMP with respect to an ocean acidification scenario. Red arrows highlight processes which yield a carbonate gap, blue arrows highlight negative feedbacks yielding the resumption of carbonate production and burial, and the grey arrow shows a feedback process which might yield a carbonate gap irrespective of acidification. (Greene et al., 2012).

propose a two-phase response in the atmospherehydrosphere system to increased CO₂-input. During the first 1-100 kyr, there will be a biocalcification crisis and carbonate dissolution in the seafloor, due to ocean acidification (Greene et al., 2012). At Lorüns, this period is probably represented by the deposition of the siliciclastic Lower Schattwald Beds. This is followed by a million-year long interval of chemical carbonate precipitation, which can buffer an increase in alkalinity (Pálfy et al., 2021). As alkalinity increases, the subtidal, lagoonal carbonate production returns, which is reflected in the deposition of the Lorüns oolite (McRoberts et al., 1997). Fig. 21 summarises the cascading effects of CAMP with respect to an ocean acidification scenario and highlights the importance of acidification for the extinction and in creating the global carbonate gap around the ETE (Greene et al., 2012).

6.4 Palaeoenvironmental reconstruction of the Lorüns section

During the latest Rhaetian, the environment at Lorüns was a shallow-marine sea, where carbonate depositions occurred at normal marine salinities. The dominance of wackestone and packstone in the Zirmenkopf Member of the Kössen Formation indicates that water energy was mostly low to moderate. In this late Rhaetian carbonate platform organisms flourished and had good living conditions. This can be deduced based on the common occurrences of bivalve fragments, echinoderms, calcareous algae, foraminifera, gastropods, and sponge spicules in many of the samples. Due to the high abundance of fossils, conditions were likely oxic in the Kössen Formation.

The onset of deposition of the Lower Schattwald Beds in the late Rhaetian, marked an abrupt shift from carbonate to siliciclastic sedimentation. This lithological shift could be related to the ETE biotic crisis and could reflect a worldwide interruption of carbonate production linked to ocean acidification (Greene et al., 2012; Hautmann, 2012; Kiessling & Danelian, 2011) (see section 6.3). Other factors that could have influenced the lithological shift are increased influx of terrigenous material and clay due to a shift towards a hotter and more humid climate (Fig. 21) and inhibition of carbonate production by eutrophication (Pálfy & Zazjon, 2012). The whole Lower Schattwald Beds and the lower part of the Upper Schattwald Beds are nearly devoid of any fossils, which implies that marine organisms were severely affected by the ETE biotic crisis at Lorüns. This fossilbarren interval, which in my study reaches to the lower part of the Upper Schattwald Beds, has also been identified at Lorüns and Kuhjoch by McRoberts et al. (1997) and Hillebrandt et al. (2013) and is highlighted in Fig. 11b as the "Extinction interval". Sediments in the Lower Schattwald Beds are mostly siltstones or calcareous siltstones, which often contain lithoclasts derived from the Kössen Formation. Some of the sediments are oxidised, which indicates oxygenated conditions and highlights that dysoxia or anoxia likely were no major killing mechanisms for marine organisms at Lorüns during the ETE.

The Upper Schattwald Beds are characterised by a return to carbonate deposition. This is coupled to a global transgression, possibly caused by the opening of the Central Atlantic Ocean (Peace et al., 2020). The lowermost limestones of the Upper Schattwald Beds are still fossil-poor mudstones, but fossil frequency increases upsection, which indicates a recovery of marine organisms after the ETE. The increase in fossils is concomitant with an increase in water energy as the mudstone shifts towards wackstone and packstone further up in the Schattwald Beds. Clay minerals and quartz appear in several of the samples from the Upper Schattwald Beds. This indicates that there was still significant terrestrial input into the depositional area and that the setting of the Lorüns was proximal during this period.

The full recovery from the ETE is marked by the development of the Hettangian massive Lorüns oolite, which mainly consists of oolite and oncoidal grainstone/packstone. This lithology is indicative of a shallow-marine, saline, warm-water environment with relatively high water energy. Felber et al. (2015) explained the development of the Lorüns oolite by an increase in the carbonate saturation state after the ETE biotic crisis and high-energy conditions due to the ongoing transgression.

The Hierlatz Limestone records a further deepening of the water at Lorüns, also coupled to the transgression after the ETE and synsedimentary faulting (Mandl, 2000). This is highlighted by a high diversity of crinoids, indicative of an early phase of drowning of Jurassic shallow water carbonate platforms (Jach, 2005), and the return to packstone/wackestone, which indicates more quiet conditions than in the Lorüns oolite. The Adnet Formation, with its typical ammonitico rosso facies, has not been investigated with thin sections but has been interpreted earlier as a deeperwater deposit by Kindle (1991) and Furrer (1993).

6.5 LA-ICP-MS results

6.5.1 Evaluation of Mn, Sr and weathering proxies

To test an eventual detritic origin of the elements measured and the influence of diagenesis on them, I made several cross-plots between Li, Ti, Si, Al, Mn, Sr and Al (sensu Kovács et al., 2020). Fig. 22 shows these cross-plots and the correlation coefficients (R^2) after linear regression. For the correlations with Mn the two spots considered to be of detritic origin (Lo23a 2 and Lo23a 3) are excluded in the crossplots. As can be seen from Fig. 22a and c, Mn and Sr show very low correlation with Al, which means that most of the Mn and Sr was not of detritic origin. Sr also shows low correlation with Mn (Fig. 22b). The correlation between Sr and Mn is positive rather than negative, which means that Sr/Mn does not follow the diagenetic trend outlined by for example Li et al. (2013). The weathering proxies Li, Ti, and Si show higher correlations with Al, and Li and Si even correlate well with Al (\mathbb{R}^2 -values ~0.68 and ~0.62) (*Fig.*

22d, e, f). A good correlation between the weathering proxies indicates that they are applicable as proxies for continental marine influx due to changes in the conti-

nental weathering rate at Lorüns (Kovács et al., 2020; von Strandmann et al., 2019).



c)

Fig. 22. Cross-plots between proxies for the origin and diagenesis of carbonates and Al, and between weathering proxies and Al. Linear regression line and the measure of correlation (\mathbb{R}^2) are also shown in the plots. a) Mn vs Al plot, b) Sr vs Mn plot c) Sr vs Al plot, d) Li vs Al plot, e) Ti vs Al plot, f) Si vs Al plot.

6.5.2 Mineralogical composition

The majority of the spots analysed with LA-ICP-MS show a mol % MgCO₃ <4, which means that they consist of low-Mg calcite or aragonite. Six spots had >4 mol % MgCO₃, which implies that they consist of higher Mg-calcite. The spots with elevated MgCO₃content were from coated grain nuclei and cortices, bioclasts, and matrix, but were all detected in only two samples: Lo53 and Lo60. Both of these samples are dolomitised, which indicates that dolomitisation might have elevated the mol % MgCO₃ in these spots. Hence, the high mol % MgCO₃ in some of the spots could be explained by diagenetic processes rather than by changes in the mineralogy of the carbonates. For the bioclasts, the elevated mol % MgCO₃ might also be influenced by their specialised biomineralisation. Sr values are uniformly low in all samples (average $264 \pm$ 152 ppm), which means that samples consist of low-Mg calcite rather than aragonite, where Sr-values are expected to be much higher. This means that the sea was calcitic during the ETE and its recovery. These results are in contradiction with the model of Hardie (1996) and Stanley & Hardie (1998), who argue that the Upper Triassic and lowermost Jurassic should be an "aragonite" sea, where ooids are mainly of aragonitic composition. Their idea is supported by studies from fluid inclusions in halite made by Lowenstein et al. (2001) and Horita et al. (2002), although these studies lacked data from the T-J transitional interval. Sandberg (1983) and Hautmann (2006) argue that the shift from an "aragonite sea" to a "calcite sea" already occurred in Late Triassic or Early Jurassic times, implying that low-Mg calcitic ooids can be expected at Lorüns. Low Sr values around a few 100 ppm are common for ancient marine limestones, according to Flügel (2010) (see "Background"). The Sr values for all the coated grains are very similar, highlighting the similar chemical conditions in the water at Lorüns.

6.5.3 Weathering

Both the Si+Al and Ti diagrams suggest a decrease in weathering rates from the Schattwald Beds to the Lorüns oolite. This decrease is confirmed by the petrographic analysis from this study, where most of the siliciclastic and clay minerals are recorded in the Schattwald Beds. A possible explanation of this weathering decrease could be the deepening of the Lorüns section or a greater distance to the siliciclastic input zone. Investigations based on clay minerals from Pálfy & Zazjon (2012) at the Kendlbachgraben section in the NCA show that the detrital component increases significantly in the boundary mudstone above the last limestone beds of the Kössen Formation, due to a humid climate with intensive terrigenous input. Above the boundary mudstone, they observed a decrease of the detrital component and a shift from a dominant clay to a dominant quartz component. Pálfy & Zazjon

(2012) explain this decrease of the detrital material by a shift towards a less humid and hot climate after the extreme greenhouse conditions caused by volcanism around the TJB. An upsection decrease in weathering was also observed in this study, but a shift from a dominant clay to quartz component in weathering was not investigated.

Based on climate models, Goddéris et al. (2008) noted an increase of weathering in the latest Triassic. They coupled this pattern to the northward movement of Pangaea during this period, increasing the amount of continental area within the equatorial humid belt, which would have enhanced silicate weathering. These results are confirmed by Schaller et al. (2015). Shen et al. (2022) noted an interval of enhanced chemical weathering of ~2 Ma around the ETE as a direct consequence from the CAMP volcanism and stated that high-latitude continental settings are more sensitive to shifts in weathering intensity than low/middle-latitude sites. This means that increased weathering during the Rhaetian and ETE was probably of global extent and dependent on both CAMP emissions and plate tectonics.

In the upper part of the Lorüns oolite (Lo64 and Lo66), Si values are below detection limit in several spots, indicating that the clay component completely dominated weathering during this period. Mineralogical analysis of quartz and clay minerals at Lorüns would assist in pinpointing the dominant weathering shifts at Lorüns.

6.5.4 Redox

As already mentioned in the "Background" the use of Mn as a redox proxy is debated (Calvert & Pedersen, 1993; Takahashi et al., 2014). In this study, Mn was used as redox proxy due to its non-detritic origin at Lorüns and because of its biogeochemical cycling across redox boundaries around the sediment-water interface (Canfield et al., 1993).

Mn values indicate dysoxic conditions in the Schattwald Beds and the lower part of the Lorüns oolite. The Ce-anomaly shows values above or close to 1 for all samples, indicating that there was no anoxia at any time during the deposition of the Lower Schattwald Beds and the Lorüns oolite. Oxygenated conditions are also supported by the low values of the euxinic proxy Mo (<0.5 ppm in coated grains) (Herrmann et al., 2012; Neubert et al., 2008;), the anoxic proxy U (<3 ppm in coated grains) (De Carlo et al., 2015; Hamelin et al., 1991; Shen & Dunbar, 1995) and the almost complete absence of the reliable anoxic proxy Re (Smrzka et al. 2019) (Appendix 3).

Hofmann et al. (2015) proposed that sediment anoxia in the Early Triassic, after the end-Permian mass extinction, could correspond to the collapse of biogenic sediment mixing during the Early Triassic and the extinction of bioturbators. The seawater anoxia might therefore only reflect poor sediment oxygenation due to the loss of the mixed layer in the water. In the Lorüns section, most of the preserved faunal groups are epifaunal, which could make the theory for the loss of the mixing layer, from Hofmann et al. (2015) for the end-Permian mass extinction also applicable for the dysoxic conditions detected in the Schattwald Beds and the Lorüns oolite. This theory is strengthened by McRoberts & Newton (1995) who observed that infaunal bivalve taxa suffered more than epifaunal bivalves during the ETE, possibly because they had aragonitic shells, whereas the epifaunal bivalves had predominantly calcitic outer shell layers (Hautmann, 2012). The dysoxia at Lorüns is therefore likely a local effect in the sediments in an otherwise oxygenated water column and did not significantly delay biotic recovery.

Krystyn et al. (2005) argue that the Schattwald Beds are a regional stratigraphic indicator of oxidised facies, due to their hematite-content. Indeed, several of the samples from the Schattwald Beds analysed in this study were oxidised. An explanation for the dysoxic conditions in the oxidised lithology of the Lower Schattwald Beds could be that the ooid, analysed with LA-ICP-MS, was allochthonous and eroded into a siliciclastic shore-environment together with the Kössen-type wackestone as discussed in section 6.1. Hence, the dysoxia could be pre-extinctional and might be coupled to possible dysoxic intervals in the sediments during the late Rhaetian. The origin of the ooid is impossible to know based on only the thin sections, so these conclusions are not settled.

6.5.5 REE + Y plots

The REE + Y-plot of the ooid cortex from the Schattwald Beds shows a negative Ce-anomaly, pronounced MREE enrichment and a significant higher amount of REE/Ys as compared to the average REE/Y -content from the ooid and oncoid cortices of the Lorüns oolite. The elevated amount of REE/Y in the Schattwald Beds compared to the Lorüns oolite can be prescribed to REE/Y enrichment during early diagenesis. REE/Y enrichment is also seen in the cement of the Schattwald Beds, strengthening a diagenetic cause for the enrichment. MREE enrichment has been prescribed to manganese oxides (Smrzka et al., 2019) and the presence of phosphates derived from phosphate mineral weathering (Hannigan & Sholkovitz, 2001). Mn shows elevated values in one nucleus (Lo23a 1) from the Schattwald Beds, so there might be a potential connection with MREE enrichment. No elevated P -values were recorded in the ooid cortex from the Schattwald Beds. However, phosphate minerals might still be present in the siliciclastic matrix of the Schattwald Beds or the Kössen Formation, which may elevate the levels of MREE encountered in the ooid cortices. This could be further investigated by mineralogical analysis.

The average REE/Y-content from the ooid and oncoid cortices of the Lorüns oolite follow each other closely and show a pronounced Ce-anomaly, Yanomaly and HREE enrichment. This pattern is consistent with the typical shale normalised pattern of seawater (Smrzka et al., 2019). Li et al. (2017) prescribe a seawater-like REE/Y pattern of Lower Triassic ooids to original precipitation of the ooids in seawater, a high-energy siliciclastic-free growth environment, rapid growth of ooid laminae and early diagenetic recrystallisation and stabilisation of ooid cortices. These factors are not directly contradicted by the results of this study, meaning that they also might control the formation of the Early Jurassic Lorüns oolite. The close correlation between the ooid and oncoid cortices in the Lorüns oolite, shows that there are no major differences in REE/Y-elemental uptake between these two different coated grains. *Fig.* 17b shows that the cortoids also display very similar amounts of REE/Y compared to oncoids and therefore to the ooids in the Lorüns oolite. This means that the LA-ICP-MS has recorded a good marine signal for the Lorüns oolite, which was not affected by any diagenetic overprint.

6.6 Comparison with measurements from the Arab Emirates

Urban et al. (submitted) and Greiff (2021) have performed LA-ICP-MS measurements in two localities (Wadi Milaha and Wadi Ghalilah) on micritised, radial and concentric ooids in the Ghalilah Formation in the Arab Emirates. Like the Lorüns section, the Ghalilah Formation contains sediments from the Upper Triassic until the Lower Jurassic, which makes it interesting for comparison with Lorüns. Table 1. shows the average mol % MgCO₃, Mn values, Ti values, Zn values, and Sr values in post-extinction ooid cortices from Lorüns, Wadi Milaha (Urban et al., submitted) and Wadi Ghalilah (Greiff, 2021) from the recovery period of the ETE. As can be seen from the table, all ooid cortices at all localities, show an average mol % MgCO₃ < 4 and very low Sr values, implying that the ooids not only are low-Mg calcitic at Lorüns, but also in the Arab Emirates. The low-Mg calcitic seas around the ETE can therefore be assumed to occur globally, or at least Tethys-wide. Hence, the model from Hardie (1996) and Stanley & Hardie (1998), who propose an "aragonite" sea in the latest Triassic/Early Jurassic, is wrong around the ETE. Mn and Ti are higher for the micritised, concentric and radial ooids from the Arab Emirates compared to the micritised ooids from Lorüns. These differences could be ascribed to differences in palaeoenvironmental conditions and depositional location. Higher Mn in the Arab Emirates as compared to Lorüns might indicate more dysoxic conditions in the Arab Emirates and higher Ti could imply higher weathering rates in the Arab Emirates. Zn was the only element, which had higher values in Lorüns than the Arab Emirates, but because the localities have very similar values if the standard deviation is considered, no further emphasis will be put on explaining this difference. The micritised ooids at Lorüns and Wadi Milaha show similar values, when considering the standard deviation, for Mn, Zn, Sr and mol % MgCO₃. For Ti the difference between the localities is larger but because of the very high standard deviation at Wadi Milaha (~157 ppm) this might not be of major significance.

Ooid types might also explain some of the differences between Lorüns and the Arab Emirates. Micritised ooids from Lorüns and Wadi Milaha have lower Mn values than concentric and radial ooids in the Arab Emirates. When considering the standard deviation, micritised ooids from Lorüns and Wadi Milaha also show lower or similar Ti values compared to the concentric and radial ooids from the Arab Emirates. For the rest of the elements and MgCO₃ the values are not clearly lower for the micritised ooids. Concentric ooids have lower elemental values than radial ooids at Wadi Milaha and Wadi Ghalilah.

The REE/Y-graphs for Wadi Milaha and Wadi Ghalilah are all MREE enriched and most of them do not show pronounced Ce- or Y-anomalies (Greiff, 2021). This REE/Y-pattern resembles the one from the ooid cortex in the Schattwald Beds. The Ce-anomaly analysed by Greiff (2021) shows a slight increase in anoxia in the Arab Emirates after the onset of the Hettangian. This can be compared to the slightly dysoxic conditions in the Hettangian lower part of the Lorüns oolite and the early-Hettangian anoxia observed in for example Germany, Luxembourg (Richoz et al., 2012), Italy (Jost et al., 2017) or Britain (Atkinson & Wignall, 2019). Likely, the simultaneous dysoxic conditions in the Arab Emirates and Europe are coupled to the environmental disturbances after the ETE.

6.7 Location of the TJB at Lorüns

The location of the TJB at Lorüns has been determined by McRoberts et al. 1997 and Felber et al. (2015). McRoberts et al. (1997) argue that the TJB is located as a sequence boundary at the top of a palaeosol, below the upper part of the Schattwald Beds. The reason for this is, according to McRoberts et al. (1997), the occurrence of a Hettangian macrofauna in the Upper Schattwald Beds. During this time, the GSSP of the Jurassic system was not yet defined, meaning that the TJB also coincided with the "ETE-peak". Felber et al. (2015) place the TJB at the base of the Lorüns oolite, based on the occurrence of ammonites. Their study was performed after the definition of the GSSP for the Jurassic system, when the understanding of the TJB was greater. Therefore, the TJB location of Felber et al. (2015) has also been used in this study of the Lorüns section.

To better define the TJB and evaluate the ecosystem turnover at Lorüns, McRoberts et al. (1997) and Felber et al. (2015) also did carbon isotope studies $(\delta^{13}C_{carb})$ on the locality. Their resulting curves are presented in Fig. 23a and b. As can be seen from the figure, the curve from McRoberts et al. (1997) shows almost constant values throughout the whole section except for a pronounced negative excursion in the BB (Boundary Beds, which is another term for the Lower Schattwald Beds), which they interpret either as a result from primary precipitation of caliche or a shortlived decrease in primary productivity. Felber et al. (2015) identified the "initial CIE" in the Lower Schattwald Beds and the "main CIE" in the basal Lorüns oolite. Both are separated by a positive excursion in the Upper Schattwald Beds. Felber et al. (2015) claim that the exact position of the main CIE is unclear. Due to the large differences in the carbon isotope curves from McRoberts et al. (1997) and Felber et al. (2015) and the ambiguity regarding the location of some of the excursions from Felber et al. (2015), further studies of the carbon isotopes at Lorüns are greatly needed.

Table 1. Comparison of the average values of mol % MgCO ₃ , Mn values, Ti values, Zn values and Sr values in ooid corti-
ces from the Lorüns section (Lo), Wadi Milaha (WM) and Wadi Ghalilah (WG). Colours indicate different types of ooids;
micritised ooids are highlighted in red, concentric ooids are highlighted in blue, and radial ooids are highlighted in orange.

Ooid type and locality	MgCO ₃ (%mol)	Mn (ppm)	Ti (ppm)	Zn (ppm)	Sr (ppm)
Micritised (Lo)	1.80	54.8	16.3	5.36	200
Micritised (WM)	1.26	86.6	161	4.44	592
Concentric (WM)	1.46	120	87	2.6	285
Concentric (WG)	1.54	299	273	3.42	271
Radial (WM)	1.70	270	280	3.5	295
Radial (WG)	1.95	385	430	3.98	283



Fig. 23. Carbon isotope curves from Lorüns by McRoberts et al. (1997) (a) and Felber et al. (2015) (b). BB means Boundary beds and refers to the Lower Schattwald Beds.

7 Conclusions

This thesis offers a detailed sedimentological and geochemical description of the Lorüns section in the Austrian Alps, which can be used for comparison with other Triassic-Jurassic boundary successions around the world. The importance of the Lorüns section lies in the continuous sedimentation from the late Rhaetian to the Sinemurian, which gives the direct possibility to study environmental conditions before, during and after the ETE. Furthermore, it might also be a key section for comparing $\delta^{13}C_{carb}$ -isotopes and other events and boundaries, like the "ETE-peak" or TJB, with other sections. The most important conclusions drawn from this study are:

- The lithology of the Hettangian Lorüns oolite shifts between an ooid-dominated grainstone/ packstone and an oncoid-dominated packstone. Cortoids are present in all samples from the Lorüns oolite.
- The depositional environment of the lower Lorüns oolite (Lo53-Lo55) was a back-shoal environment, dominated by oolite grainstone/ packstone, containing oncoids. Between Lo56 and Lo60 the depositional environment was

lagoonal, because of the presence of oncoids in oncoidal/oncolite packstones but absence of ooids. The depositional environment shifted back to a back-shoal environment in the upper part of the Lorüns oolite (Lo61-Lo66), due to the return of oolite grainstone/packstone containing oncoids. Deposition of the Lorüns oolite occurred in shallow-marine waters of the upper euphotic zone. These waters were warm and saline and located in the tropics or lower subtropics, but not very near to the equator. Precipitation of coated grains was likely favoured by an increase in the marine carbonate saturation state after ETE biotic crisis and high energy conditions due to a global transgression in the Early Jurassic.

- There were no major differences in element incorporation between ooids, oncoids and the cortoid.
- A majority of the ooids and oncoids analysed with LA-ICP-MS have a mol % MgCO₃ <4 and very low Sr values (average ooid cortex: $200 \pm$ 83.2 ppm, average oncoid cortex: 211 ± 43.0 ppm), which implies that the sea at Lorüns was low-Mg calcitic during the latest Rhaetian and early Hettangian. Measurements from Urban et al. (submitted) and Greiff (2021) indicate a low -Mg calcitic sea in the Arab Emirates around

the same time as in Lorüns. This means that the low-Mg calcite signal recorded in Lorüns is of global, or at least Tethys-wide extent. Hence, the model by Hardie (1996) and Stanley & Hardie (1998), who propose an "aragonite sea" in the Late Triassic and Early Jurassic is wrong in this time interval.

- A mol % MgCO₃ > 4 was only detected in samples which were dolomitised (Lo53 and Lo60). Therefore, the elevated levels of MgCO₃ can be prescribed to early diagenetic dolomitisation, rather than changes in the environment at Lorüns.
- Weathering rates are the highest in the Schattwald Beds and decrease in the Lorüns oolite. The decrease in weathering can be coupled to a deepening of the Lorüns section and a greater distance to the silicilastic input zone. It can also be related to a less humid and hot climate after the extreme greenhouse conditions caused by volcanism around the ETE.
- The seawater at Lorüns was oxygenated during the late Rhaetian and early Hettangian. Dysoxia probably occurred in the sediments of the Lower Schattwald Beds (Lo23a) and lower part of the Lorüns oolite (Lo54) and is prescribed to the loss of biogenic sediment mixing coupled to the extinction of infaunal taxa during the ETE. Recorded dysoxia in the oxidised lithology of the Schattwald Beds might be explained by a potential origin of the ooid from the Schattwald Beds in the Kössen Formation. This environment would also be more favourable for ooidformation than the siliciclastic Schattwald Beds.
- The ooid from the Schattwald Beds is MREEenriched and has a considerably higher REE/Ycontent than the average ooids and oncoids from the Lorüns oolite. MREE-enrichment can be explained by the possible presence of manganese oxides and phosphates in the sample, and the high REE/Y-content can be related to the siliciclastic lithology of the sample. The averaged REE/Y-content is very similar for ooids and oncoids of the Lorüns oolite and they follow the HREE-enriched pattern of normal seawater.
- The lack of calcareous fossils during the extinction, the deposition of the siliciclastic Schattwald Beds during the ETE, and the formation of coated grains in the Lorüns oolite indicate that ocean acidification occurred at Lorüns, especially affecting acid-sensitive taxa.

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Appendix 1

Pictures showing the grains and the spots analysed with LA-ICP-MS.


























































Appendix 2

Pictures of all the thin sections in PPL.



Lo5 (a) and Lo8 (b)



Lo11 (a, b)



Lo14 (a) and Lo17 (b)



Lo19 (a, b)



Lo23a (a, b)



Lo23b (a) and Lo25 (b)



Lo29 (a) and Lo33 (b)



Lo34 (a) and Lo39 (b)



Lo40 (a) and Lo41 (b)



Lo44 (a, b)



Lo46 (a) and Lo50 (b)



Lo51 (a, b)



Lo52 (a, b)



Lo53 (a, b)



Lo54 (a, b)



Lo55 (a, b)



Lo56 (a, b)



Lo57 (a, b)



Lo58 (a, b)



Lo59 (a, b)



Lo60 (a, b)



Lo61 (a, b)



Lo62 (a, b)



Lo63 (a, b)



Lo64 (a, b)



Lo65 (a, b)



Lo66 (a, b)



Lo67 (a, b)



Lo68 (a, b)

Appendix 3

Values of Li, Al, Si, P, Ti, V, Zn, Mo, Ba and U in coated grains from the Lorüns section. The samples are presented for each coated grain in stratigraphic order from left to right.

































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