



- 1 Precipitation of dolomite from seawater on a Carnian coastal plain (Dolomites, northern
- 2 Italy): evidence from carbonate petrography and Sr-isotopes
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Abstract. The geochemical conditions conducive to dolomite formation in shallow evaporitic 13 environments along the Triassic Tethyan margin are still poorly understood. Most of the 14 15 Triassic dolomites in the Austroalpine and the South Alpine realm are affected by late 16 diagenetic or hydrothermal overprinting, but recent studies from the Carnian Travenanzes Formation (South Alpine) provide evidence of primary dolomite. Here a petrographic and 17 geochemical study of the dolomites intercalated in a 100-m-thick Carnian sequence of distal 18 alluvial plain deposits is presented to gain better insight into the conditions and processes of 19 dolomite formation. The dolomites occur as 10- to 50-cm-thick homogenous beds, mm-scale 20 21 laminated beds and nodules associated with palaeosols. The dolomite is nearly stoichiometric with slightly attenuated c-reflections. Sedimentary structures indicate that the initial primary 22 dolomite or precursor phase consisted largely of unlithified mud. Strontium isotope ratios 23 (<sup>87</sup>Sr/<sup>86</sup>Sr) of homogeneous and laminated dolomites reflect Triassic seawater, suggesting 24 precipitation in evaporating seawater in a coastal ephemeral lake or sabkha system. However, 25 the setting differed from modern sabkha or coastal ephemeral lake systems by seasonally wet 26 27 conditions with a significant siliciclatic input and inhibition of significant lateral groundwater





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- 28 flow through impermeable clay deposits, thus representing a non-actualistic system in which
- 29 dolomite formed along the ancient Tethyan margin.

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- 31 Keywords Dolomite, Sr-isotopes, sabkha, alluvial plain, peritidal platform, Travenanzes
- 32 Formation, ephemeral lake, authigenic carbonate.

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#### 35 1 Introduction

36 The formation of dolomite  $[CaMg(CO_3)_2]$  under Earth surface conditions in modern and ancient environments is still a major unsolved problem in sedimentary geology. Dolomite 37 does not precipitate from modern open ocean water, apparently, because its nucleation and 38 39 growth is inhibited by a high kinetic barrier. For the same reason its precipitation under 40 laboratory conditions has been difficult (cf. Land, 1998), and therefore the factors that may 41 have influenced dolomite formation through Earth history, giving rise to a significant part of the sedimentary record, also remain poorly constrained. Van Tuyl (1916) discussed several 42 43 competing theories, one of which was the chemical theory, where dolomite is a primary 44 precipitate, hence, forming as a result of the conditions prevailing in the depositional environment. In contrast, stable isotope and fluid inclusion data often indicate that massive 45 46 dolomites formed due to replacement of precursor calcium carbonate during burial diagenesis, 47 i.e., at higher temperature and under conditions decoupled from the ancient depositional environment. Chilingar (1965) suggested that the portion of dolomite in carbonates increases 48 with geological age, implying a replacement during burial. However, burial dolomitization 49 50 requires a mechanism pumping large volumes of Mg-rich water through porous rock (Machel, 2004) and is not always a viable process. There is evidence that at certain times in Earth's 51 52 history, large amounts of dolomite could have formed under near-surface conditions (penecontemporaneous dolomite), and several studies linked the abundance of dolomite to 53





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secular variations in seawater chemistry, with preferred dolomite formation during times of "coloite seas" (Civen and Wilkinson, 1987; Worren, 2000; Burns et al., 2000)

"calcite seas" (Given and Wilkinson, 1987; Warren, 2000; Burns et al., 2000).

In the Tethyan realm, penecontemporaneous dolomite formation seems to have prevailed 56 during the Triassic (Meister et al., 2013, and references therein), in an "aragonite sea", while 57 elsewhere dolomite was not particularly abundant (cf. Given and Wilkinson, 1987). In Norian 58 shallow water dolomites of the Dolomia Principale, Iannace and Frisia (1994) measured 59 oxygen isotope values as positive as +3.5‰, suggesting a formation at Earth surface 60 temperatures, whereas dolomites of the overlying early Jurassic units typically show 61 signatures of burial diagenetic overprint. Frisia et al. (1994) interpreted these dolomites to be 62 an early diagenetic replacement of precursor carbonate. In a recent study, Preto et al. (2015) 63 suggested that the dolomites of the Carnian Travenanzes Formation (Fm.) in the Venetian 64 Alps are primary precipitates, i.e. they precipitated directly from a solution in the sedimentary 65 environment and not by replacement of a precursor phase during burial. This interpretation is 66 based on high-resolution transmission electron microscope (HR-TEM) analysis showing 67 nanometre-sized crystal aggregates within single micron-scale dolomite crystals. The nano-68 crystal structures were not replaced by any of the dolomite phases described by Frisia and 69 Wenk (1993) in Late Triassic dolomites of the Southern Alps, and they show similarity to 70 dislocation-ridden Mg-rich phases observed in modern sabkha dolomite and interpreted as 71 primary (Frisia and Wenk, 1993). This finding is intriguing, not only because it is consistent 72 73 with primary dolomite formation already discussed by Van Tuyl (1916) and observed in many modern environments (e.g., Sabkha of Abu Dhabi: Illing, 1965; Wenk et al., 1993; unlithified 74 dolomite is also mentioned in Bontognali et al., 2010; and Court et al., 2017; Deep Springs 75 76 Lake, California: Jones, 1965; Clayton et al., 1968; Meister et al., 2011; Coorong Lakes: Von der Borch, 1976, Rosen et al., 1989, Warren et al., 1990; Brejo do Espinho, Brazil; Sánchez-77 Román et al., 2009; Lake Acigöl, Turkey: Balci et al., 2016; Lake Neusiedl, Austria: 78 79 Neuhuber et al., 2015; Lake Van: McCormack et al., 2018), but it also provides a window into





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ancient primary dolomite formation pathways. This finding is also consistent with recent experiments by Rodriguez-Blanco et al. (2015), demonstrating a nano-crystalline pathway of dolomite nucleation and growth. Critically, nanometre size nuclei show a different surface energy landscape compared to macroscopic crystals, allowing for potentially lower energy barriers, perhaps modified by organic matter, microbial effects, clay minerals or particular water chemistry, and thus, promoting a spontaneous precipitation of dolomite.

The interpretation of primary dolomite in the Travenanzes Fm. needs further validation by 86 nano- and atomic scale analyses and further petrographic and geochemical investigations to 87 establish the environmental and geochemical conditions on this Carnian platform. In 88 particular, the origin of ionic solutions conducive to dolomite formation is still unclear. 89 Comparison with modern environments shows that ionic solutions may either be seawater-90 derived, as shown for the sabkhas along the Persian Gulf coast, where several hydrological 91 mechanisms were discussed (Adams and Rhodes, 1960; Hsü and Siegenthaler, 1969; 92 McKenzie et al., 1980, McKenzie, 1981; see Machel, 2004, for an overview; cf. also Teal et 93 94 al., 2000), or derived from continental groundwater, as shown for the coastal ephemeral lakes of the Coorong area (Australia; Alderman and Skinner, 1957; Von der Borch et al., 1976, 95 Rosen et al., 1989; Warren et al., 1990). While both types of fluid become concentrated 96 during evaporation and, perhaps, modified by the precipitation of carbonates and evaporites, 97 giving rise to abundant dolomite formation, it remains unclear which mechanism prevailed on 98 99 the Carnian platform.

The Travenanzes Fm. differs from these potential modern analogues in its large amounts of clay. In fact, dolomites occur in the Travenanzes Fm. as beds intercalated in a 100-m-thick sequence of red clay, deposited on a distal alluvial plain, presumably under seasonally wet conditions. This facies shows, except for the horizons containing marine fossils, striking similarity to a Germanic Keuper facies, which represents an extended and entirely continental playa lake system, also showing intercalations of primary dolomite in red clay (Reinhardt and





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Ricken, 2000). Although the Travenanzes Fm. is clearly located, palaeogeographically, in the Tethyan depositional region (Breda and Preto, 2011), its facies separation from a Germanic Keuper facies may not be precisely coincident with palaeogeographic features, such as the Vindelician high zone. We suggest that the composition and origin of ionic solutions conducive to primary dolomite formation, either from continental water or seawater, is also an indicator for the palaeogeographic separation between the two facies zones.

Here we provide a detailed investigation of dolomites of the Travenanzes Fm. to 112 reconstruct the processes and factors conducive to dolomite formation. We specifically 113 searched for sedimentary structures indicating that the initially deposited authigenic carbonate 114 was still unlithified, as it would be expected if it spontaneously precipitated from the shallow 115 water bodies of ephemeral lakes or tidal ponds. Radiogenic Sr isotope ratios  $(^{87}Sr)^{86}Sr)$  were 116 117 measured in the dolomites and compared with the known Triassic seawater Sr-isotope curve (Veizer et al., 1999; McArthur et al., 2012) to determine if the ionic solutions conducive to 118 dolomite formation are derived from seawater or from continental runoff. Values were also 119 120 compared to dolomites from modern environments and to dolomites of clear continental origin from the Germanic Keuper. Based on the new insights we discuss possible scenarios of 121 dolomite formation that could have prevailed along the Triassic western Tethys margins and 122 in similar evaporative environments. 123

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#### 125 **2** Geological setting

The Dolomite mountains (Southern Tyrol and Venetian Alps; Fig. 1a) are well known for their characteristic peaks consisting of Triassic carbonate platform limestones and dolomites. These platforms developed all along the margins of the western Tethys ocean (Stampfli and Borel, 2002), and are separated by deep basins in the middle Triassic and form an extended coastal plain during the Carnian and Norian. The Adriatic plate rotated by almost 90° counter clockwise during alpine orogeny (Ratschbacher et al., 1991; Handy et al., 2010). As a result,





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132 the deep-water environments are found to the north in today's tectonic position although they 133 were originally located to the east (Fig. 1a). In the Dolomites, the Triassic paleogeography was largely preserved in spite of Alpine deformation because the Dolomites form a ca. 60 km 134 wide pop-up structure bound by the periadriatic line to the north and northwest and the 135 Valsugana fault to the southeast (Fig. 1a, inset). Therefore, the Dolomites were never buried 136 137 to greater depth and have not experienced a metamorphic overprint (Doglioni, 1987). The colour alteration index of conodonts in the Heiligkreuz Fm., underlying the Travenanzes Fm. 138 in this region, is 1, suggesting maximum burial temperatures of less than 50°C which are 139 confirmed by biomarker data (Dal Corso et al., 2012). 140

The Travenanzes Fm. lies unconformably above the Heiligkreuz Fm., and is overlain by 141 the Dolomia Principale (Hauptdolomit) with a transgressive boundary (Fig. 1b). Presumably 142 as a result of a change in climate and increasing humid episodes during the Carnian, large 143 amounts of siliciclastic material were deposited, entirely filling the more than 100 m deep 144 basins between the carbonate platforms of the Cassian dolomite (Gattolin et al., 2013; 2015). 145 These basin-filling deposits form a coastal succession or mixed carbonate siliciclastic ramp, 146 including large clinoforms with sandstones and conglomerates (Heiligkreuz Fm.; see Preto 147 and Hinnov, 2003; Gattolin et al., 2013; 2015). The overlying Travenanzes Fm. was deposited 148 on an extremely flat topography, as it consists of ca. 100-m-thick red and green claystone with 149 intercalated dolomites, evaporites and siliciclastic beds (Fig. 2; Kraus, 1969; Breda and Preto, 150 151 2011). In a south-north transect, it shows a typical interfingering between alluvial deposits 152 with conglomerates and sandstones to the south and a carbonate-dominated peritidal to sabkha facies to the north (Breda and Preto, 2011). The upper boundary to the Dolomia Principale is 153 154 time-transgressive, i.e., it becomes younger from north to south. The Travenanzes Fm. consists of three transgressive-regressive cycles, with the highstand deposits showing 155 identical peritidal carbonate facies as the Dolomia Principale (Breda and Preto, 2011). The 156





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boundary to the Dolomia Principale is defined by the last occurrence of siliciclastic material

158 (Gianolla et al., 1998).

The depositional environment of the siliciclastic facies in the Travenanzes Fm. has been 159 interpreted as a dryland-river system by Breda and Preto (2011). Such a system occurs in arid 160 environments if rivers drain into a coastal alluvial plain, but do not reach the coast. 161 Evaporation along the way may lead to the formation of playa lakes, whereas on the seaward 162 side extended evaporative tidal areas, i.e., sabkhas, develop. Both types of environment are 163 well known for giving rise to modern dolomite formation (see references above). As the 164 Southern Alps were located in tropical latitudes, a warm arid climate, perhaps influenced by a 165 monsoon effect, had developed (Muttoni et al., 2003). Rivers provided large amounts of clay, 166 becoming partially oxidized under subaerial conditions, a typical red and green clay 167 succession containing palaeosols developed. 168

This facies is widespread throughout the Alpine and Tethyan realm during the Carnian, but the same deposits are strongly deformed by alpine tectonics in most Austroalpine units, forming a characteristic band of rauhwacke, the "Raibl beds" (e.g., Czurda and Nicklas, 1970). In the Travenanzes Fm. the entire sequence still shows its depositional architecture, providing a pristine archive to study the diverse intercalated dolomites.

The Carnian and Norian deposits of the Keuper in the endorheic Germanic Basin show a similar facies as the Travenanzes Formation. The Germanic deposits are described in more detail by Reinhardt and Ricken (2000; and references therein), and they clearly represent continental playa lake deposits. Here they are only included for comparison with the Travenanzes Formation.

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#### 180 3 Methods

#### 181 **3.1 Petrographic and mineralogical analysis**

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182 A total of 39 hand specimens were collected from the stratigraphic section at Rifugio Dibona 5 km west of Cortina d'Ampezzo (46.532727N/12.067161E; Fig. 1; Breda and Preto, 183 2011). Additional samples of Triassic dolomites from the Germanic Basin (Weser Fm. and 184 Arnstadt Fm. near Göttingen, Northern Germany) and modern dolomite from the Coorong 185 Lagoon (South Australia) and Deep Springs Lake (California) were also analysed for 186 187 comparison. Polished thin sections were carbon coated for analysis under the scanning electron microscope (SEM) using a FEI Inspect S-50 SEM (Thermo Fisher Scientific, 188 Bremen, Germany). Element contents were determined semi-quantitatively using an EDX 189 detector (EDAX Ametek, New Jersey, United States) under high vacuum, a spot size 5.0 and 190 12.5 kV beam voltage at a working distance of 10 mm. Differences in mineralogy at the 191 192 micron scale were mapped in backscatter mode with high contrast.

193 For bulk mineralogical analysis three dolomite samples were milled with a disk mill. Clay mineralogy was determined on 40 g aliquots that were leached two times for 24 h in 250 ml of 194 25% acetic acid to dissolve all carbonate (Hill and Evans, 1965). The clay mineral separates 195 196 were washed three times with H<sub>2</sub>O and centrifuged. The grain size fraction  $<2 \mu m$  was collected by sedimentation in an Atterberg cylinder after 24 h 33 min. Oriented samples were 197 prepared by pipetting the suspensions (10 mg clay/ml) on glass slides and analysed after air 198 drying. To identify expandable clay minerals, the samples were additionally saturated with 199 ethylene-glycol and heated to 550°C (Moore and Reynolds, 1997). X-ray diffraction analysis 200 201 of bulk samples and clay mineral separates was performed with a PANalytical X'Pert Pro diffractometer using CuKa radiation with 40 kV and 40 mA. The samples were scanned from 202 203  $1.76^{\circ}$  to  $70^{\circ}$   $2\vartheta$  with a step size of  $0.0167^{\circ}$  and 5 s per step. The X-ray diffraction patterns were interpreted using the Panalytical software "X'Pert High score plus" and Moore and 204 Reynolds (1997) for the clay minerals. 205

Total organic carbon (TOC) and total inorganic carbon (TIC) contents were determined for seven samples of pure claystone, not containing any dolomite layers or nodules. This material





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213	3.2 Carbon and oxygen isotope analysis
212	
211	ramp of 70°C per min to a maximum temperature of 1000°C.
210	Department of Environmental Geosciences at the University of Vienna, with a temperature
209	g of dry sample powder was measured in a LECO RC-612 multiphase carbon analyser, at the
208	was used as carbonate-free control for acid leaching experiments as explained below. Ca. 0.2

Carbon and oxygen isotopes were measured on 28 samples which where micro-drilled 214 215 from thin section cuttings (see below). The samples were analysed with a Delta V Plus mass spectrometer coupled to a GasBench II (Thermo Fisher Scientific, Bremen, Germany) at the 216 ETH Zürich (Zürich, Switzerland) following the procedure described in Breitenbach and 217 Bernasconi (2011). The precision was better than 0.1% for both isotopes. The oxygen isotope 218 values were corrected for kinetic fractionation during dissolution of dolomite in anhydrous 219 phosphoric acid at 70°C, using a fractionation factor of 1.009926 (Rosenbaum and Sheppard, 220 1986). 221

222

## 223 **3.3 Element analysis**

Total element concentrations were measured in leachates of the same three dolomite 224 specimen analysed by XRD and two claystones with the lowest inorganic carbon content. The 225 purpose of these measurements was to test the efficiency of the sequential extraction 226 227 procedure used for Sr-isotope analysis, and to determine potential origins of the Sr. The samples were homogenized in an agate pestle and mortar and 100 mg of the homogenized 228 powder were weighed into centrifuge tubes. The samples were reacted in 10 ml 0.1 N acetic 229 230 acid and placed on a shaker for two days. The sample was centrifuged and the supernatant 231 was stored separately. The leaching step was repeated with 10 ml of 1 N acetic acid. Five ml of each fraction were used for element concentration analysis (the rest was further processed 232 233 for Sr-isotope analysis; see below). The solutions were evaporated on a heating plate and the





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residues were redissolved in 5 ml 2.5 N HNO<sub>3</sub>. This step was repeated with 5 ml 5% HNO<sub>3</sub>. Concentrations were measured with a Perkin Elmer 5300 DV ICP-OES at the Department for Environmental Geosciences (University of Vienna). Detection limits for the different elements in rock ( $\mu$ mol/g) were: Al: 0.185, Ca: 0.025, Fe: 0.090, K: 0.026, Mg: 0.041, Mn: 0.002, Na: 0.004, P: 0.032, Ti: 0.002, Ba: 0.001, Sr: 0.001 and Rb: 0.012. The precision of the measurements (relative standard deviation; RSD) for the elements Al, Ca, K, Mg, Ti, Ba and Sr was  $\leq 0.9\%$  and for the elements Fe, Mn, Na, Rb, P it was  $\leq 6.8\%$ .

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## 242 3.4 Radiogenic Sr-isotope analysis

To ensure that Sr from the pure dolomite phase is extracted specific areas free of clay 243 minerals were recognized by SEM and identified using an Olympus SZ61 microscope 244 245 equipped with a MicroMill sampling system (Electro Scientific Industries). Eleven samples were drilled over a square area of 5-10 mm<sup>2</sup>, or along a line in laminated rocks, to a depth of 246 247 350 μm. To prevent the powder from being blown away, the samples were drilled within a drop of MilliQ-H<sub>2</sub>O, and the suspension was transferred to a centrifuge tube using a pipette. 248 249 Also bulk samples, clay samples, pure celestine and barite purchased from W. Niemetz 250 (Servitengasse 12, 1090 Vienna, Austria), pure dolomite powder from Alfa Aesar (Thermo Fisher - Kandel - GmbH, Postfach 11 07 65, 76057 Karlsruhe, Germany) and a fragment of a 251 252 single dolomite crystal were analysed as controls. They were crushed to a powder in an agate 253 mortar and pestle. Dolomite, barite, and celestine were mixed in a similar ratio as they occur 254 in the dolomites of the Travenanzes Fm. and run through the entire procedure as a control of extraction efficiency. 14 mg of rock powder was weighed out for isotope analysis. 255

As additional precaution to extract the most pure dolomite phase for Sr-isotope analysis, a sequential extraction was used. The extractions were routinely performed in 2 ml or 15 ml polypropylene tubes with cap at room temperature on a shaker for 10 min to 24 h. The following leaching reagents (always 2 ml) were used: 1 M NaCl, 3.3 M KCl, 0.1 N acetic





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acid, 1 N acetic acid and 6 N HCl. Each reaction step was repeated once, and the residues
were washed with 2 ml of MilliQ H<sub>2</sub>O after each step to remove remains of the previous
solvent.

Sr was separated from interfering ions (e.g. Fe, K, Rb and Ca) using an ion exchange column packed with BIO RAD AG 50W-X8 resin (200-400 mesh, hydrogen form). Leachates were evaporated, dissolved in 6 N HCl and 2.5 N HCl and loaded to the column in 2 ml 2.5 N HCl. Then 51 ml of 2.5 N HCl were run through the column to wash out the interfering ions. The Sr was eluted with a further 7 ml 2.5 N HCl and dried after collection. Total procedural blanks for Sr were <1 ng and were taken as negligible (the amounts of strontium in the samples were always higher than 100 ng).

The isotopic composition of Sr was measured with a Triton (Thermo Finnigan) thermal 270 ionisation mass spectrometer. Sr fractions were loaded (dissolved in 1  $\mu$ l H<sub>2</sub>O) as chlorides 271 and vaporized from a Re double filament. The double filament configuration was used to 272 accelerate detachment of the Sr from the filament. The cup configuration was calibrated such 273 274 that masses 84, 85 (centre cup), 86, 87 and 88 are detected. The NBS987 Sr isotope standard (number of replicates = 40) shows a  ${}^{87}$ Sr/ ${}^{86}$ Sr-ratio of 0.710272 ±0.000004 during the time of 275 investigation, with the uncertainty of the Sr isotope ratios quoted as  $2\sigma$ . Interference with <sup>87</sup>Rb 276 was corrected using a <sup>87</sup>Rb/<sup>85</sup>Rb ratio of 0.386. Within-run mass fractionation was corrected 277 for  ${}^{86}\text{Sr}/{}^{88}\text{Sr} = 0.1194$ . 278

279

#### 280 4 Results

## 281 4.1 Petrographic description of dolomites

Fig. 2 shows the distribution of the different types of dolomite through the 100-m-thick lower, clay-rich interval of the Travenanzes Fm., above which the facies switches sharply to massive bedded dolomites similar to those of the overlying Dolomia Principale. Macroscopically three types of dolomite can be distinguished: homogenously bedded





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286 dolomite, laminated dolomite, and nodular dolomite (Fig. 3a-c). The lower and middle part of 287 the clay-rich series harbours mainly homogeneous dolomite beds in red clay. Between 40 and 70 m several horizons with gypsum nodules occur (Fig. 3d). A 30-cm-thick fluvial 288 conglomerate with dolomite-cemented quartzarenites and pebbles of ripped up micritic 289 290 carbonate occurs at 75 m (Fig. 3e), above which palaeosols with dm-scale vertical peds, 291 possible root traces showing green reduction haloes, and nodular dolomite (calcic vertisols; cf. Cleveland et al., 2008), are more frequent (e.g., Fig. 3b). Tempestite beds with 292 megalodonts, foraminifers and ostracods occur at 65 and 89 m. A pronounced transition 293 occurs in the uppermost ca. 8 metres of the clay-rich interval (Fig. 2b), where the clay entirely 294 changes from red to grey colour (Fig. 2c), and laminated dolomites become predominant 295 296 while evaporites and palaeosols are absent. The laminated dolomites (Fig. 3c) and cm- to dmscale dolomite-clay interlayers show intense slumping and soft sediment deformation and 297 pseudo-teepee structures (Figs. 3f, g). Here we provide a short summary of the petrographic 298 analysis of thin sections of the different types of dolomite with the most important features 299 300 compiled in table 1.

301

# 302 Homogenous dolomites

Homogeneous dolomite beds are usually 10 cm to 50 cm thick, embedded within clays and 303 with sharp, plane-parallel joints. They consist of dolomicrite, which was described as 304 305 aphanotopic dolomite by Breda and Preto (2011), according to the extended nomenclature for dolomite fabrics by Randazzo and Zachos (1983). The sediment is matrix-supported and 306 contains irregular, partially rounded mud clasts (intraclasts) that consist of an aphanotopic 307 308 dolomite as the matrix. Some of the mud clasts contain smaller and somewhat darker mudclasts or peloids (Fig. 4a, arrow). Soft sediment deformation is often not clearly visible 309 due to the homogeneous structure of the mud, but it can be observed where the mud clasts are 310 deformed within the matrix (Fig. 4b). Some of the homogeneous beds in the lower part of the 311





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312	section show	sub-millimetre	lamination	that is	only	visible	under	the	microscope,	where	it

appears as an alternation of light (locally coarser) and dark aphanotopic dolomite.

The clay content in the homogeneous beds is generally low. A few beds (e.g. at 33.5 m in

the section) consist of silty or sandy dolomite, as reflected in a high abundance of detrital

quartz in thin section. Pseudomorphs after gypsum occur in a dolomite bed at 120 m (Fig. 4c,

d). Moldic porosity occurs in three layers at 43, 65 and 89 m, within aphanotopic dolomite.

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318 These are the tempestite beds observed in the outcrop (cf. Breda and Preto, 2011).
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One homogenous dolomite bed located at 64 m in the section contains oolithic grainstone, lacking both an aphanotopic and a cement matrix (Fig. 4e). Ooids are either hollow (where the cores may have been dissolved) or filled with sparite and are surrounded with an isopachous cement rim.

323

#### 324 Nodular dolomites

Nodular dolomites (Fig. 3b) often occur in beds of vertical peds linked to palaeosols as indicated by horizons of typical vertical cracks showing green alteration fronts. Single nodules also may sporadically occur embedded within metre-thick beds of red and green clay. Nodules are usually 5 to 10 cm in size, consist of aphanitic dolomite or occasionally somewhate coarser microspar, and in cross section show both red and pale areas. Most nodules also show a deformed or brecciated internal structure with the interstices between the clasts mostly consisting of matrix and clay cutans.

332

## 333 Laminated dolomites

Laminated dolomites occur in the upper part of the clay rich interval, between 90 and 110 m in the section (Fig. 4f-i). In the field, they show an alternation of light grey dolomite laminae and dark grey to black clay laminae in the mm-range. Some dolomite laminae show upward bending reminiscent of pseudo-teepee structures (Fig. 4f), and the space within the





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338 teepee is sometimes infilled with sparry cement. Also, the bending of the laminae towards the 339 upward directed cuspids is reminiscent of load structures (dish structures), but they also may represent desiccation cracks. The laminae are frequently ripped apart and fragments of 340 laminae occur reworked as flat pebbles embedded in an aphanotopic dolomite matrix (Fig. 341 4g). Some laminae show a microsparitic appearance and laminar fenestral porosity. In some 342 laminae a peloidal fabric is observed (e.g in Fig. 4f). Laminae are typically graded, whereby 343 the upper part is darker, indicating an increase in the clay content (Fig. 4h, i). The top of the 344 laminae is often truncated by an erosion surface, and rip-up clasts of the fine mud (mud 345 clasts) are embedded in the overlying coarse layer. Some laminated dolomites contain 346 continuous layers with inclusions of celestine crystals in the 100-µm-range, some of them 347 with barite in their centre (Fig. 5a-c). Occasionally also pyrite occurs. 348

Under the SEM, laminated dolomites show an anhedral structure in the 1-5 µm range. No 349 350 difference in mineral structure and grain size is usually observed between mud clasts and the surrounding, often lighter-coloured matrix. Dolomite crystals at the margins between 351 dolomite and clay interlayers often coalesce into 5-um-scale round aggregates consisting of 352 353 several subhedral crystals with different orientation (Fig. 6a, b; the crystals show orientation 354 contrast under BSE mode). Dolomite crystals are often porous, showing a somewhat disordered appearance, but they are surrounded by syntaxial rims. In most cases, the rims 355 entirely fill the intercrystalline space, forming almost hexagonal compromise boundaries (Fig. 356 357 6c, d). These rims occur both in homogeneous and laminated dolomites.

358

## 359 Germanic Keuper dolomites

A sample from the Carnian Lehrberg Beds (middle Lehrberg bed; clay pit Friedland, 12 km south of Göttingen, Northern Germany; Seegis, 1997; Arp et al., 2004) shows a brittle structure with high porosity. The material consists mainly of packed ooids or rarely peloids in





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363	a sparitic cement matrix. Under the SEM, subhedral to euhedral dolomite in the 5- $\mu$ m-range
364	are observed within the ooids (not shown).
365	A sample from the Norian Arnstadt Fm. (formerly termed "Steinmergelkeuper"; middle
366	grey series; locality of Krähenberg, 11 km SSW of Göttingen, Northern Germany; Arp et al.
367	2005) shows a mm-scale lamination and cm- to dm-sized laminated clasts, which were
368	interpreted as a stromatolite breccia. The laminae contain abundant agglutinated siliciclastic
369	grains (mainly quartz, subordinate albite) and phosphoritic fish scales. The dolomicrite shows
370	a subhedral structure in the $\leq 5 \ \mu m$ range with a few larger subhedral grains resulting in a
371	porphyrotopic fabric (not shown).

372

#### 373 4.2 Mineralogy

Bulk dolomite shows a position of the 104 peak at a mean d-value of 2.88816 Å (Fig. 7a; Table 2). This indicates a Ca content of 50.7%, based on the equation of Lumsden (1979). The structural order is indicated by the ratio of the superlattice-ordering peak at (015) to the (110) ordering peak. The height ratio is 0.44, which is near to 0.519 (Table 2) indicated for an ordered dolomite in the Highscore database.

Clay mineral analysis (Fig. 7b-d) revealed illite in samples TZ14-1 and TZ14-7 and an R3 ordered illite-smectite mixed-layer clay mineral in sample TZ14-9. In the ethylene-glycolsaturated state, the broad shoulder at 11.4 Å contains components of the illite 001 reflection and of the fourth order of a 47 Å superstructure peak whose unit cell consists of three 10 Å illite layers and one 17 Å smectite layer (Moore and Reynolds, 1997). This smectite component was not observed in samples TZ14-1 and TZ14-7.

385

#### 386 4.3 Carbon content

Total carbon contents in shales (Table 3) range from 0.06 to 0.51 wt%. Samples TZ16-1 und TZ16-19B showing the lowest TIC of 0.02 wt% were selected as controls to test for





#### Sr-isotopes in Carnian primary dolomite

- <sup>87</sup>Sr/<sup>86</sup>Sr-ratios of Sr potentially adsorbed to clay minerals. TOC-contents are in the range of
- 390 0.05 0.16 wt%. Max. TIC-values are 0.46 wt%.

391

# 392 4.4 Carbon and oxygen isotopes

393 Carbon isotope values vary between -3.38 and +4‰ VPDB. Oxygen isotope values are 394 between -0.7 and +0.9% VPDB (three outliers show values as low as -1.5% VPDB; Table 4; 395 Fig. 8a). A clear distinction occurs between nodular dolomites showing negative  $\delta^{13}$ C-values and homogeneous dolomites showing positive values. Laminated dolomites show 396 397 intermediate values and low variability. The oxygen isotopes show an upward increasing trend (Fig. 8b). The calculated temperature of formation assuming a Triassic seawater 398 composition of -1% VSMOW using the fractionation equation of Vasconcelos et al. (2005) 399 400 shows temperatures between 29 and 39°C. A more positive value of the water would result in 401 higher temperatures.

402

#### 403 **4.5 Element composition of the dolomites**

404 Concentrations of the elements Al, Ca, Fe, K, Mg, Mn, Na, P, Ti, Ba, Sr, and Rb (mmol/g sample) are shown in Table 5. Ca contents are between 1.68 and 2.33 mmol/g in the 0.1 N 405 acetic acid fraction and between 2.71 and 2.87 mmol/g in the 1 N acetic acid fraction. Mg 406 407 contents are between 1.61 and 2.34 mmol/g in the 0.1 N acetic acid fraction and between 2.48 408 and 2.64 mmol/g in the 1 N acetic acid fraction. Based on these concentrations, the amount of dolomite dissolved is between 30 and 43 wt% of the bulk sample in the 0.1 N acetic acid 409 fraction and between 49 and 52 wt% in the 1 N acetic acid fraction of the sequential 410 extraction. In total, between 84 and 90 wt% of the bulk sample were dissolved during these 411 two extraction steps. If molar concentrations of Ca are plotted vs. Mg a linear trend with a 412 413 slope of 0.935 is observed (Fig. 9a), indicating 48.3 mol% MgCO<sub>3</sub> in the dolomite phase.





## Sr-isotopes in Carnian primary dolomite

414	The Sr-concentrations in bulk dolomite samples are in the range of 0.38 and 1.16 $\mu$ mol/g
415	in the 0.1 N acetic acid fraction and between 0.57 and 0.79 $\mu mol/g$ in the 1 N acetic acid
416	fraction (except one extremely high value of 34.91 $\mu$ mol/g in sample TZ14-9). These contents
417	are much higher than in pure clay mineral samples with 0.047-0.417 $\mu mol/g$ in the 0.1 N
418	acetic acid fraction and even lower concentrations (<0.19 $\mu$ mol/g) in the other fractions. In
419	all samples measured by ICP-OES, rubidium (Rb) concentrations are below the detection
420	limit of 0.012 µmol/g.

421 Correlation of Sr contents to other elements did not show clear trends. In particular, Sr422 content did not correlate with Mg or Ca. Sr correlates with K (Fig. 9b), but at the same time,
423 K is extremely low in all clay mineral leachates.

424

# 425 4.6 Sr-isotopes

# 426 <sup>87</sup>Sr/<sup>86</sup>Sr-ratios of pure minerals

Results of Sr-isotope measurements are listed in Table 6. Repeated extractions of chemically pure dolomite reference material dissolved in 0.1 N acetic acid showed a range of  $^{87}$ Sr/ $^{86}$ Sr-ratios between 0.709942 ±0.000011 and 0.710831 ±0.000007. Pure single crystals of dolomite extracted sequentially showed the highest value (0.708401 ±0.000040) in the 1 M NaCl fraction. Values in the 0.1 N acetic acid fraction (0.707735 ±0.000006) and the 1 N acetic acid fraction (0.707666 ±0.000006) are lower by almost 0.001 than in the NaCl fraction.

In pure barite,  ${}^{87}$ Sr/ ${}^{86}$ Sr-ratios decrease by about 0.0013 in the extraction sequence from 0.1 N acetic acid to 6 N HCl. Celestine is highly soluble and was only measured in the 1 M NaCl fraction and one time in 0.1 N acetic acid. It shows similar values as in the 1 M NaCl fraction of the pure barite-celestine-dolomite mixture (0.708038 ±0.000003), but the latter increased to 0.709501 ±0.000040 in the 0.1 N acetic acid fraction.





Sr-isotopes in Carnian primary dolomite

#### 439

440 <sup>87</sup>Sr/<sup>86</sup>Sr-evolution during sequential extraction of dolomites of the Travenanzes Fm.

Different modifications of the sequential extraction were investigated using three samples (TZ14-1, TZ14-7 and TZ14-9; Table 6).  ${}^{87}$ Sr/ ${}^{86}$ Sr-ratios decrease in sample TZ14-1 from 0.708125 ±0.000012 to 0.707666 ±0.000004 with increasing strength of the leaching reagent, while the values remain almost constant in sample TZ14-9. However, repeating the 0.1 N acetic acid extraction (for 36 h) after a rather intense first extraction (4h, 12h, 4h) resulted in extremely high values (0.715417 ±0.000250 in TZ14-1 and 0.7192266 ±0.000455 in TZ14-9). Standard deviations are also higher than in the other fractions.

The sequential extractions were repeated, whereby the Sr-concentrations were determined by ICP-OES (see section above). In addition, 1 N acetic acid and 6 N HCl fractions were extracted. Results are similar to the previous extraction sequences, but the values further decreased in the 1 N acetic acid fraction. Only the HCl-fraction showed very high values of  $0.730453 \pm 0.000005$  in sample TZ14-7.

453 Sequential extractions of the clay samples from the Travenanzes Fm. show a similar 454 increase with the sequential extraction steps from 0.1 N acetic acid fraction to 6 N HCl, where 455  ${}^{87}$ Sr/ ${}^{86}$ Sr-ratios reach similar values as in the dolomite extracts (from 0.722998 ±0.000018 to 456 0.733910 ±0.000024).

457

# 458 <sup>87</sup>Sr/<sup>86</sup>Sr-ratios in micro-drilled dolomite

Eleven dolomite samples were micro-drilled from areas where dolomite was most pure based on examination by SEM and dissolved in 0.1 N acetic acid. The values of the Travenanzes Fm. are in the range of  $0.707672 \pm 0.000003$  to  $0.707976 \pm 0.000004$ . The highest value occurs in a dolomite nodule, while no systematic difference between homogenous and laminated dolomite was observed. Dolomite of the Germanic Keuper samples shows much higher <sup>87</sup>Sr/<sup>86</sup>Sr-ratios of  $0.709303 \pm 0.000006$  and  $0.709805 \pm 0.000005$ , respectively.





Sr-isotopes in Carnian primary dolomite

#### 465

- 466 <sup>87</sup>Sr/<sup>86</sup>Sr-ratios of modern dolomites (Deep Springs Lake, Coorong Lakes)
- 467 Dolomites of Deep Springs Lake show strongly radiogenic values of  $0.713086 \pm 0.000004$ 468 and  $0.713207 \pm 0.000004$ , which are much higher than modern seawater values, showing a 469  ${}^{87}$ Sr/ ${}^{86}$ Sr-ratio of  $0.709234 \pm 0.000009$  (DePaolo and Ingram, 1985). In contrast, dolomite from 470 the Coorong Lakes (Milne Lake) shows ratios between  $0.709251 \pm 0.000004$  and 0.709275471  $\pm 0.000003$ , which is very near to modern seawater. Different incubation times (5 min und 10 472 h) in 0.1 N acetic acid had no influence on the isotope ratios.

473

# 474 5 Discussion

# 475 5.1 Interpretation of microfacies within different types of dolomite

#### 476 *Homogeneous dolomite beds*

The homogeneous dolomite beds, which are mainly intercalated in the lower, clay-rich part 477 of the Travenanzes Fm., consist of fine-grained dolomicrite (aphanotopic dolomite), with 478 479 occasional intraclasts of the same aphanotopic dolomite as the matrix. Soft sediment deformation and dolomicrite infill between mud clasts indicate that this sediment consisted to 480 a large extent of unlithified carbonate mud. Based on the abundance of fine mud, water 481 energy was probably not very high (Demicco and Hardie, 1994), although reworking and 482 partial rounding of the mud clasts require at least occasionally higher water energies. 483 According to the standard microfacies concept this type falls into SMF 23 ("non-laminated 484 485 homogeneous micrite and microsparite without fossils"), indicating a deposition in "saline and evaporative environments, e.g. in tidal ponds" (Flügel, 2010). Also, SMF 24 ("lithoclastic 486 487 floatstones, rudstones and breccias") is observed in some of the beds where mud clasts are abundant. These facies types are consistent with supersaturation-driven precipitation of a fine-488 grained authigenic carbonate in environments partially restricted from open seawater and 489 490 would match both with a coastal sabkha environment and/or with shallow ephemeral lakes.





## Sr-isotopes in Carnian primary dolomite

Ephemeral lakes may have formed on extended coastal alluvial plains along the Tethyan
margin during the Carnian. The fine mud may have been homogenized and redistributed due
to minor wave action in the ponds (cf. Ginsburg, 1971).

In a semi-arid climate, episodic flooding of the alluvial plains by river water, which 494 however mostly evaporated before reaching the coast, led to the formation of a dryland river 495 system (Breda and Preto, 2011). The fluvial system may have supplied water to temporally 496 existing evaporating ponds. Alternatively, the alluvial plain may have been sporadically 497 flooded by seawater, explaining the intercalations of authigenic dolomite layers in the 498 succession of alluvial clays. Homogeneous dolomites show a positive carbon isotope 499 signature between 0.7 and 4‰ VPDB (except one outlier), which would be consistent with 500 formation from unaltered marine carbon in evaporative brine, with no significant contribution 501 502 of <sup>12</sup>C derived from organic matter. As indication of evaporative conditions, several gypsum 503 beds occur between 45 and 70 m in the section, and pseudomorphs after gypsum were observed in a thin section of a dolomite at 120 m (Fig. 4c, d). But evaporites may not always 504 be preserved as they were most likely dissolved due to seasonally wet conditions. 505

While most homogeneous dolomite beds consist of aphanitic dolomite, a bed of dolomitic 506 ooid grainstone devoid of matrix occurs at 64 m (Fig. 4e), and tempestites showing moldic 507 porosity indicative of dissolved allochems and dissolved fossils occur at several levels in the 508 section. These beds must represent events of higher water energy, contributing sediment from 509 510 more open marine areas. The presence of marine fossils, such as Megalodon, indicate that at 511 least episodically the environment was marine influenced. The microfacies of the oolite falls 512 into SMF 15, which indicates proximity to the seaward edge of the platform. A similar facies, however, is encountered in the Carnian Lehrberg Beds (Seegis, 1997) in a lacustrine setting. 513 Several beds containing abundant siliciclastic material (mainly angular quartz clasts) are more 514 likely due to a riverine flooding event, providing detrital material from the continent. Thus, 515





#### Sr-isotopes in Carnian primary dolomite

- the microfacies in homogenous dolomite beds indicates both marine and continental influence
- 517 on the depositional environment.
- 518
- 519 Laminated dolomite

In the upper part of the clay-rich interval, predominantly laminated dolomites reminiscent 520 521 of loferites (Fischer, 1964) occur. The change from more homogeneous to laminated dolomite intercalations correlates with the change from red to dark grey clay. The lamination consists 522 523 of millimetre-scale dolomite/clay interlayers suggesting an alternation of clay and fine dolomite deposition. The microfacies falls into SMF 25 ("laminated evaporite-carbonate 524 mudstone facies") indicating an "upper intertidal to supratidal sabkha facies in arid and 525 semiarid coastal plains and evaporitic lacustrine basins" (Flügel, 2010). Laminae showing soft 526 527 sediment deformation could not be attributed to stromatolitic bindstone facies (SMF 19 to 21). Only some layers showing a coarser fabric with interstitial dolosparite or dolomicrosparite 528 containing putative peloids have been interpreted as microbial laminites (Preto et al., 2015). 529 530 Mostly, graded bedding indicates a direct sedimentation process rather than in situ precipitation of the primary carbonate within a microbial mat (Vasconcelos et al., 2006; 531 Bouton et al., 2016; Court et al., 2017; Perri et al., 2018). A detrital origin of the clay in the 532 dolomites is confirmed by the well-ordered illite-smectite mixed-layer composition which 533 would be atypical for authigenic clay minerals. Frequent subaerial exposure and desiccation 534 535 may explain why the sediment was not homogenized and the lamination is preserved. This is supported by the occurrence of pseudo-teepee structures as remnants of desiccation cracks. 536 Rip-up clasts were formed during subsequent flooding, whereby angular flat pebbles occur 537 where the sediment was desiccated or partially lithified. However, laminae also show 538 frequently plastic deformation (e.g. in Fig. 3g) where the mud was still unlithified. 539

540 Some uncertaintly exists as to whether the facies was peritidal or represents ephemeral 541 lakes, as suggested for the homogeneous dolomites above. Episodic high water-energy





## Sr-isotopes in Carnian primary dolomite

542 indicated by the rip-up clasts, combined with frequent desiccation, could point to evaporative 543 tidal conditions, as they occur in a sabkha. What is atypical for a modern sabkha is the large amount of detrital input. But this is owed to the seasonally wet conditions during the Carnian 544 and the facies can be considered a mixed facies of alluvial plain and coastal sabkha: a "dirty" 545 sabkha. Under such conditions, the large amounts of evaporites, in particular gypsum, as they 546 547 usually occur in a sabkha, could have been dissolved. Why the occurrence of laminated dolomites coincides with the transition from red to grey clays is not clear but may be related 548 to more permanently water-saturated conditions in the subsurface, while the surface was 549 exposed to periodic desiccation. Also this would be consistent with a sabkha environment. 550

551

# 552 Nodular dolomite

The clay beds were subject to strong evaporation and vadose diagenesis causing oxidation 553 and red colour. This generally indicates, at least seasonally, arid conditions. Dolomite nodules 554 that occur sporadically within certain intervals show internal brecciation, which probably 555 556 occurred after sedimentation. Internal brecciation is a typical feature of present day calcretes in arid environment (e.g. Mather et al., 2018). Slightly negative  $\delta^{13}$ C-values indicate a 557 558 contribution of carbon derived from organic matter degradation, suggesting that they formed within the sediment. Presumably the formation of dolomite nodules could be related to 559 560 diagenesis in palaeosols. In the upper part of the section (between 80 and 105 m) dolomite 561 nodules are associated with green reaction haloes along vertical peds in palaeosols of vertisol-562 calcisol type (Preto et al., 2015). Carbonate formation may have been related to reducing fluids in water-logged soils during humid intervals, while the crack formed during desiccation 563 in dry periods, perhaps facilitated by the presence of expandable clay minerals (smectite). 564

565

#### 566 **5.2** The origin of ionic solutions conducive to dolomite formation

567 Overall, the dolomites in the Travenanzes Fm. show facies that match a variety of potential





## Sr-isotopes in Carnian primary dolomite

568	depositional environments. They show some similarity to the Germanic Keuper, and it is not
569	entirely clear from the facies, whether a marine influence occurred, except if indicated by
570	marine fossils, as in the tempestite beds. To better trace the origins of ionic solutions to the
571	environments that were conducive to dolomite formation, Sr-isotopes were analysed.
572	

573 Strontium derived from seawater

Radiogenic <sup>87</sup>Sr/<sup>86</sup>Sr ratios can be indicative of the source of ionic solutions from which the 574 dolomite precipitated (Müller et al., 1990a; Müller et al., 1990b). Sr-isotopes in selected 575 dolomites through the Travenanzes Fm. at the Dibona section showed values between 576 0.707672 ±0.000003 and 0.707976 ±0.000004. We correlate the Dibona section (Fig. 10) with 577 the Carnian seawater curve (Korte et al., 2003). Although the age interval of the Travenanzes 578 Fm. is not precisely constrained, findings of ammonites at the base of the succession suggest a 579 Tuvalian II age (subbullatus zone, 232.5-231.0 Ma; Ogg, 2012). The upper boundary of the 580 Travenanzes Fm. is time-transgressive and hence the age not precisely constrained. We 581 582 assume that the sedimentation rate was at least as high, or higher, than in the peritidal carbonates of the Dolomia Principale. In this region, the Dolomia Principale includes a part of 583 the Rhaetian (Neri et al., 2007) and, thus, its upper boundary is near the Triassic-Jurassic 584 boundary at 201.3 Ma. The seawater curve was fixed at the lower boundary of the 585 Travenanzes Fm. and the time axis was varied to fit the seawater curve parallel to the 586 envelope of minimal <sup>87</sup>Sr/<sup>86</sup>Sr-ratios measured in the dolomites (Fig. 10). The base of the first 587 massive dolomite at 110 m in the profile would then have an age of approximately 229 Ma. 588

589 Comparison with the seawater curve shows that the dolomites of the Travenanzes Fm. have 590 largely marine <sup>87</sup>Sr/<sup>86</sup>Sr-ratios (Fig. 10). Only values from micro-drilled samples most gently 591 extracted with 0.1 N acetic acid were used for this reconstruction, and the resulting values all 592 lie within a range of 0.00022 with the seawater values (grey shaded area). This scatter 593 towards more positive values, compared to seawater, may be due to a small influence of





# Sr-isotopes in Carnian primary dolomite

continental water. Indeed, during deposition of the Travenanzes Fm. sufficient continental water would have been available from rivers, and ions may have become concentrated while the water was evaporating in the distal alluvial plain. Alternatively, Sr desorbed from clay minerals could have added more radiogenic values to the brine. But even if a small influence of Sr of continental origin is present, because of the much higher Sr concentrations in seawater, the marine signal is dominant.

This observation does not support the classical Coorong model for dolomite formation, 600 where alkalinity is largely derived from continental groundwater. The Coorong Lakes in 601 South Australia are ephemeral lakes largely supplied with groundwater (Von der Borch et al., 602 1975). Strangely, though, the <sup>87</sup>Sr/<sup>86</sup>Sr ratios we measured in Milne Lake (one of the Coorong 603 Lakes) show modern seawater composition (Fig. 11), but this can be explained as the local 604 605 groundwater largely originates from a Pleistocene carbonate aquifer, accordingly carrying a Pleistocene Sr-isotope signature. A similar scenario for the Travenanzes Fm. is unlikely as the 606 only large-scale preceding carbonate platforms at that time were the Late Ladinian-Carnian 607 608 Cassian dolomite platforms (Russo et al., 1997). But based on the stratigraphic context, all basins between these platforms were infilled by the Heiligkreuz Fm. and an extremely flat 609 topography had established that was stratigraphically overlain and sealed by the alluvial 610 deposits of the laterally persistent Travenanzes Formation. Furthermore, the Travenanzes Fm. 611 consists of 100 m of impermeable clay (containing expandable clays) such that a long-612 613 distance transport of groundwater can be excluded.

We conclude that the <sup>87</sup>Sr/<sup>86</sup>Sr ratios of the dolomites truly represent a dominating marine influence. Presumably, seawater was transported to the interior of the platforms by episodic flooding (spring tide or storm) events. Even in a seasonally wet climate the input of river water on Sr-isotopes was insignificant compared to the influence of ions (including Sr) from seawater that became concentrated by evaporation. Laminated dolomites in the uppermost part of the section show values most similar to seawater composition, which is consistent with





## Sr-isotopes in Carnian primary dolomite

- 620 a greater influence of peritidal conditions.
- 621

#### 622 The influence of Sr adsorbed to clay minerals

An outlier with higher <sup>87</sup>Sr/<sup>86</sup>Sr ratios occurs in a dolomite nodule, presumably representing 623 a more continental influence or perhaps more seasonally wet and evaporative conditions with 624 625 less marine influence. But also higher values may be due to contamination and partial leaching of clay minerals within the dolomite samples. Within the extraction sequence (1 M 626 NaCl  $\rightarrow$  0.1 N acetic acid  $\rightarrow$  1 N acetic acid), the <sup>87</sup>Sr/<sup>86</sup>Sr ratio generally remains constant or 627 becomes slightly less radiogenic, i.e., more similar to seawater. However, the values strongly 628 increase with leaching in 6 N HCl (Table 6). A modification of the <sup>87</sup>Sr/<sup>86</sup>Sr ratios due to 629 contamination by <sup>87</sup>Sr from the radioactive decay of <sup>87</sup>Rb to <sup>87</sup>Sr can be considered as 630 negligible since the concentrations of Rb was below the detection limit of 0.05 ppm (Table 5) 631 and the half time of the decay is 48.8 billion years. Also, an influence of celestine and Sr-rich 632 barite, observed under the SEM, on the Sr-isotope values can be largely excluded. These 633 mineral phases are bound to distinct layers of the laminated dolomites, where they could be 634 avoided by micro-drilling in areas where the dolomite was pure. Only one value in sample 635 TZ14-9 shows extremely high Sr-concentrations. This sample was micro-drilled near to a 636 celestine layer and it is therefore not surprising that a celestine crytal may have been leached. 637 The isotopic composition of the celestine is also similar to Carnian seawater. 638

In the NaCl-fraction only minimal amounts of dolomite are dissolved. The slightly more radiogenic <sup>87</sup>Sr/<sup>86</sup>Sr ratio may be derived from Sr that is lightly adsorbed to clay minerals and finely dispersed in the clay matrix, although Sr<sup>2+</sup> as a two-valent cation is more strongly adsorbed to clay mineral than Na<sup>+</sup>, and thus not easily desorbed by NaCl. With increasing extraction efficiency and purity of the carbonate phase, the values approach seawater values in the 1 N acetic acid fraction. Also, values from micro-drilled samples are generally more similar to seawater values, probably because more pure dolomite was sampled (Table 6). 1 N





# Sr-isotopes in Carnian primary dolomite

646 acetic acid is usually observed not to strongly attack interlayer ions in clay minerals.

647 Clay minerals leached in 6 N HCl show significantly more radiogenic values compared to dolomite samples (Table 6). This finding is consistent with strongly radiogenic values in the 6 648 N HCl-fraction of dolomite samples (up to 0.730453 ±0.000005) and supports that the clay 649 minerals are the carriers of a Sr-pool significantly more radiogenic than the carbonate phase 650 651 showing marine values. Sr is known to adsorb to illite-smectite mixed layer clay minerals (Missana et al., 2008). The HCl-fraction most likely includes adsorbed Sr, and Sr occupying 652 the interlayer positions of the clay minerals, and presumably also structurally bound Sr in the 653 clay mineral phase. In particular, illite-smectite mixed-layer clay minerals, as detected by 654 XRD of the clay mineral separate in sample TZ14-9 (Fig. 7d), could have two different 655 origins, burial diagenesis and continental weathering. Based on the tectonic setting and low 656 657 burial depth of the Dolomites, burial depth for smectite-illite transition has not been reached. Therefore, these minerals are most likely derived from silicate weathering, with the Sr-658 signature representing the crustal origin of the parent rock. Our finding of radiogenic Sr-659 isotope ratios supports that clay minerals did not essentially incorporate the Sr from seawater, 660 delivered at high sealevel stand. It is therefore clear that Sr extracted from the dolomites is not 661 derived from clay minerals. 662

663

# 664 Dolomite as primary archive of Sr-isotope signatures

The question is, whether Sr truly represents the conditions of dolomite formation or whether it inherits the Sr content of some precursor phase. Baker and Burns (1985) and Vahrenkamp and Swart (1990) showed very small distribution coefficients between aqueous and solid solutions, and high Sr-contents measured in Abu Dahbi sabkha dolomites (Müller et al., 1990b) may be derived from precursor aragonite. However, dolomite in the Travenanzes Fm. is largely primary (Preto et al., 2015) and thus not formed from an aragonite precursor. It is likely that remobilization of Sr during burial may have released parts of the Sr from





# Sr-isotopes in Carnian primary dolomite

#### dolomite which is now present as celestine and barite inclusions.

673 Furthermore, Sánchez-Román et al. (2011) demonstrated that protodolomite forming in culture experiments contain Sr in the range of several thousand ppm. The incorporation 674 mechanism of Sr is still not entirely clear, since Sr is a large ion that should occupy the sites 675 676 of Ca in the crystal lattice. However, in Sánchez-Román et al. (2011) Sr appears to correlate 677 with the Mg content, and another incorporation mechanism may occur, such as by surface 678 entrapment. A correlation of Sr-contents with K-contents is observed for the Travenanzes dolomites. It could be circumstantial, but would not be inconsistent with an alternative 679 mechanism of Sr-incorporation, such as surface entrapment. Even if it is taken into account 680 that only protodolomite formed in microbial culture experiments (Gregg et al., 2015), natural 681 modern dolomites are often rich in Sr (e.g. Meister et al., 2007). The Sr could occur in 682 disordered nano-structural domains that are not picked up in the bulk XRD-signal. 683 Alternative, non-classical nucleation and growth pathways, e.g. by nano-particle attachment, 684 could play a role in the abnormal partitioning of Sr in the dolomite lattice. Thus, a high Sr-685 686 content in the Travenanzes Fm. or in Abu Dhabi Sabkha dolomites is likely a true signature of primary dolomites. 687

688

# 689 5.3 Mode of dolomite formation and comparison with known models

#### 690 *Primary dolomite formation*

Several indications support that the origin of dolomite in the Travenanzes Fm. is largely primary. Formation temperatures reconstructed from oxygen isotopes and assuming Triassic seawater composition of -1‰ VSMOW are between 28 and 33°C. If a typical <sup>18</sup>O enrichment of 3‰ in a sabkha (McKenzie et al., 1980; McKenzie, 1981) is assumed, the calculated temperatures would be between 40 and 50°C, which is still within a range possible in a sakbha. Both temperature and evaporation may have changed over time, which may explain the observed linear trend in oxygen isotopes across the section (Fig. 8B). Furthermore, there is





## Sr-isotopes in Carnian primary dolomite

no co-variation between  $\delta^{13}$ C and  $\delta^{18}$ O, as opposed to evaporation in hydrologically closed 698 settings such as the Germanic Keuper basin (Reinhardt and Ricken, 2000; Arp et al., 2005). 699 700 Both oxygen isotopes and nano-crystalline structures observed by Preto et al. (2015) preclude a later pervasive recrystallization during burial diagenesis. Sedimentary structures indicate 701 that most of the homogenous dolomite and laminae containing aphanotopic dolomite was 702 703 unlithified, and dolomite was therefore deposited as fine-grained mud. This is further supported by mm-scale interlayering of clay and dolomite in the laminated dolomites near the 704 top of the sequence, and some dolomite/clay couplets showing a fining-upward bedding. 705 706 Based on the observation of nano-crystal structures, replacement did not take place and it appears logical to assume that the primary phase was already dolomite. 707

While most of the dolomite may have been primary, micron-scale interstices between the 708 709 dolomicrite grains must have been cemented after deposition. This cementation resulted in 710 rims visible under the SEM and resulting in near hexagonal compromise boundaries. The cement may have contributed <sup>13</sup>C-depleted carbon during early diagenesis. The lowest  $\delta^{13}$ C 711 values of -3.4% VPDB occur in the nodules. There is no indication that these nodules formed 712 at the surface. They rather formed within the sediment, probably due to reducing conditions 713 and influenced by dissolved inorganic carbon from degrading organic matter in the 714 palaeosols. Homogeneous and laminated dolomites are clearly distinct from nodules in their 715 carbon isotope compositions (Fig. 8a), indicating only a minor contribution from pore-water 716 717 derived dissolved inorganic carbon. Carbon isotope values are thus largely consistent with a primary precipitation. The mode of dolomite formation as fine mud and subsequent 718 cementation is comparable to several modern sites of dolomite formation. 719

720

#### 721 The sabkha model

The classical sabkha model involves dolomite formation under intra-supratidal conditions,
 concentration of brines through either seepage reflux (Adams and Rhodes, 1960) or





# Sr-isotopes in Carnian primary dolomite

724 evaporative pumping (Hsü and Siegenthaler, 1969; Hsü and Schneider, 1973; McKenzie et 725 al., 1980; McKenzie, 1981) and precipitation of dolomite upon increase of the Mg/Ca ratio due to gypsum precipitation (see Machel, 2004, for a more detailed discussion of varieties of 726 sabkha models). This group of models allow for a mixture of seawater and continental 727 groundwater, with seawater providing mainly the ions for dolomite precipitation. Coastal 728 729 sabkhas are typically characterized by laminated (Lofer-type) dolomites, whereby the laminae are largely still unlithified after deposition (Illing, 1965; Bontognali et al., 2010; Court et al., 730 731 2017). In fact, in the sabkha of Abu Dhabi, both pathways, via replacement of precursor aragonite and by direct precipitation of dislocation-ridden primary dolomite, were observed 732 (Wenk et al., 1993). 733

The sabkha model is thus a reasonable model for the uppermost parts of the Travenanzes section, showing laminated dolomites, marine Sr-isotope values and indications of frequent desiccation and flooding in a peritidal setting. Yet, the conditions differed from the modern sabkhas along the Persion Gulf by the large amount of alluvial clay (dirty sabkha), as opposed to aeolian sand. Most of the fine lamination then may result from periodically varying conditions, perhaps with clay deposition during episodes of fluvial discharge and carbonate deposition during evaporative conditions.

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## 742 The continental playa lake model

The playa lake model was originally suggested by Eugster and Surdam (1973) for dolomite of the Green River Formation (Wyoming), but the primary formation of fine dolomite mud is observed in many alkaline playa lakes, such as Deep Springs Lake (Peterson et al., 1963; Clayton et al., 1968; Meister et al., 2011), Lake Acigöl (Turkey; Balci et al., 2017), Lake Neusiedl (Austria; cf. Neuhuber et al., 2016), Lake Van (Turkey; McCormack et al., 2018; for an overview see Eugster and Hardie, 1978, and Last, 1990). This type of setting has also been suggested for the Germanic Keuper deposits during the late Carnian and Norian, when the





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Germanic Basin was entirely disconnected from the Panthalassa ocean and was continental (Reinhardt and Ricken, 2000). The Travenanzes Fm., with its homogeneous dolomite intercalations in red and green clays, is strikingly similar to playa-lake Keuper facies in the Germanic Basin. There, dolomite formed upon evaporation and concentration of the continental brines under semi-arid climate.

755 However, Sr-isotope data support a dominantly marine origin of ionic solutions to the Travenanzes Fm., whereas Sr-isotopes are strongly radiogenic in the Germanic Keuper 756 757 dolomites (or in Deep Springs Lake; Fig. 11). The two settings are thus fundamentally different. Even dolomite nodules, showing somewhat more radiogenic values than seawater in 758 the Travenanzes Fm., are still indicating a dominating marine influence. The slightly more 759 radiogenic influence could be due to the clay minerals present in the nodules that were 760 difficult to entirely separate from the carbonate. Also, dolomite nodules may have formed in 761 relation to palaeosols, during somewhat more humid times and, thus, may have been slightly 762 influenced by continental water input from the rivers. 763

764

# 765 The coastal ephemeral lake model (Coorong model)

The Coorong model was proposed by Von der Borch et al., 1975; Von der Borch 1976; 766 Rosen et al., 1989; see Warren, 2000, for detailed information), explaining the formation of 767 primary and uncemented dolomite in the Coorong lakes of South Australia. The isotope 768 769 values show that the contribution of ionic solutions, and hence alkalinity, of continental origin 770 to the dolomitizing fluids was minimal and that the dolomites are seawater derived. This may be distinct from the typical Coorong model, where alkalinity is provided from an inland karst 771 772 system. But other coastal ephemeral lakes exist, such as along the Brasilian coast north of Rio 773 de Janeiro. Partially unlithified dolomite occurs in Brejo do Espinho (Sánchez-Román et al., 2009), which is in fact largely similar to the Coorong lakes, but ionic solutions are largely 774 775 derived from seawater.





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A coastal ephemeral lake model would probably be most suitable to explain homogeneous dolomite beds of the Travenanzes Fm., where hypersaline ponds may have formed in a dryland river system. However, unlike the recent ephemeral lakes (such as Lagoa Vermelha, Brejo do Espinho and the Coorong Lakes) the clay-rich sediment must have inhibited groundwater flow. Hence, while modern coastal ephemeral lakes receive their water largely through seawater percolating through porous dune sand, episodic flooding with seawater must have provided ionic solutions for dolomite formation on the Carnian platform.

783

#### 784 A non-actualistic system

Overall, the depositional environment reconstructed for the Travenanzes Fm. shows 785 similarities to modern systems were dolomite forms. Among all the scenarios, a coastal 786 ephemeral lake model would be most similar to the conditions conducive to homogeneous 787 dolomites, lacking signs of frequent desiccation, while a coastal sabkha model may explain 788 the laminated intervals near the top of the studied succession. In contrast to any modern 789 790 systems, the clay rich sediments of the Travenanzes Fm. precluded any transport of groundwater, which plays a role for ionic transport in both the modern day ephemeral lake 791 model and the different versions of sabkha models. Although modern systems provide valid 792 analogues for the mechanism of dolomite formation in the past, and probably throughout 793 Earth's history, none of them is an exact environmental analogue. The Carnian alluvial plains 794 795 that covered an enormous area along the Tethys margin (e.g. Garzanti et al., 1995) represent a 796 non-actualistic system in terms of their sedimentary, hydrological and climatic conditions. Besides, the geochemistry of Tethys seawater may also have been different from today, an 797 798 issue that requires further investigation. These aspects need to be taken into account if we intend to understand the role of dolomite formation through Earth history. 799

In the light of a possible spontaneous precipitation as fine mud in the water column, perhaps via formation and aggregation of nano-particles, further discussion of a nucleation





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and growth pathway of dolomite will be necessary. While several modifiers may also play a
role in the water column, such as dissolved organic matter (Frisia et al., 2018), microbial EPS
(Bontognali et al., 2013), or suspended clay particles (Liu et al., 2018), fluctuating conditions
inducing spontaneous nucleation and growth of dolomite, in agreement with Ostwald's step
rule (Deelman, 1999), require further consideration as a factor favourable for dolomite
formation on a seasonally variable platform (Meister and Frisia, accepted).

The main finding of this study is that most of the dolomite in the >100 m thick Travenanzes Fm. probably formed through direct precipitation in a seawater-derived solution. This mode of primary dolomite formation has rarely been considered in the study of geological dolomite bodies, but may explain the genesis of many other large-scale, fine dolomite units that preserve fossils and sedimentary structures.

813

## 814 6 Conclusions

Dolomite beds intercalated in a 100-m-thick Carnian alluvial clay sequence in the Travenanzes Fm. largely formed as fine-grained primary mud. The depositional environment was minimally affected by currents and most likely prevailed as ephemeral lakes in an extended alluvial plain or dryland river system. The large amounts of clay are related to at least seasonally wet conditions. Also palaeosols and diagenetic dolomite nodules could have formed under such conditions. The facies resembles strongly those of the Triassic playa lakes prevailing in the Germanic Basin or in the modern Deep Springs Lake.

Sr-isotopes clearly show a marine signal, indicating seawater as the main source of ions. The depositional environment shows most similarities with coastal ephemeral lakes resulting in the deposition of homogeneous dolomite beds through most of the sequence, changing into a "dirty" sabkha near the top of the sequence, where fine dolomite/clay interlayers suggest alternating deposition of extremely fine authigenic dolomite from evaporating water, and clay.





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Overall, Sr-isotopes and petrographic observations provide insight into a nonuniformitarian system including both elements of coastal ephemeral lake systems and sabkhas as an environment of primary dolomite formation. Considering the precipitation of primary dolomite from coastal lakes or ponds may help explaining other dolomite deposits with preserved sedimentary features throughout geologic history.

833

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1100

#### 1101 Figure Captions

- 1102 Figure 1. (a) Palaeogeographic map of the Southern Alpine to Germanic domains during the
- 1103 middle Triassic, reproduced from Brack et al. (1999; modified). Bal: Balaton; BG: Burgundy
- 1104 Gate; Car: Carnian Alps; ECG: eastern Carpathian Gate; Lomb: Lombardy; NCA: Northern
- 1105 Calcareous Alps; SMG: Silesian Moravian Gate. Inset: Tectonic map of the Southern Alps





# Sr-isotopes in Carnian primary dolomite

1106	(Brack et al., 1996, modified) showing the sampling location at Rifugio Dibona. GL:
1107	Giudicarie Line; PL: Pustertal Line; VL: Val Sugana Line. (b) Stratigraphy of the middle to
1108	late Triassic in Venetian Alps, showing a transition in geometries from basin and platform
1109	topotraphy during the Lower Carnian to an extended alluvial to tidal plain in this Upper
1110	Carnian. The shaded area indicates the Travenanzes Fm., showing a lateral transition in facies
1111	and a transgressive boundary to the Dolomia Principale. Compiled from Breda and Preto
1112	(2011), after De Zanche et al. (1993), modified.

1113

Figure 2. Stratigraphic section at Rifugio Dibona: (a) Complete section modified after Breda and Preto (2011); (a) detailed section of uppermost part of the clay-rich interval, showing sampling locations. (c) Outcrop photograph showing the uppermost grey part of the clay-rich interval with the location of the profile shown in (b).

1118

Figure 3. Outcrop images of different types of dolomite intercalated in red and grey clay of 1119 1120 the Travenanzes Fm. at Rifugio Dibona: (a) Homogeneous dolomite bed (15 cm thick; 33 m). (b) Upper part: dolomite nodules embedded in red clay, crosscut by green coloured cracks as 1121 part of a calcic vertisol (95 m). (c) Laminated dolomite (110-112 m) in grey clay. (d) Bed 1122 with gypsum nodules, and cracks filled with gypsum, at 50 m; (e) Dolomite-cemented 1123 1124 conglomerate bed at 75 m. (f) Laminated bed showing soft sediment deformation (106 m); an isoclinal synsedimentary fold is indicated by the arrow. (g) Laminated dolomite showing 1125 folding of the laminae due to soft sediment deformation (same bed as in f). 1126

1127

**Figure 4.** Photomicrographs of thin sections of dolomites of the Travenanzes Fm.: (a) Rounded mud clasts embedded in dolomicrite matrix. The larger mm-size intraclast in the upper left side of the image (arrow) consists itself of matrix with darker embedded mudclasts (sample TZ16-St1; 104 m). (b) Mud clasts in dolomicrite matrix. Mudclasts are deformed and





# Sr-isotopes in Carnian primary dolomite

1132	layers of coarser and finer matrix are equally affected by plastic deformation (sample TZ16-
1133	22; 120 m). (c, d) Pseudomorphs after gypsum in fine-grained dolomudstone (arrows). (e)
1134	Oolitic grainstone (sample TZ14-4; 64 m). The cortices consist of microcrystalline dolomite
1135	lacking a radial structure. Some show a concentric structure (arrow). (f) Laminated dolomite
1136	showing pseudo-teepee structures (arrow). Vertical cracks are often, but not always,
1137	associated with pseudo-teepees (sample TZ14-10; 107 m). Some coarser grained laminae may
1138	contain microsparite and peloids (P). (g) Laminated dolomite showing both plastic and brittle
1139	deformation of laminae. A cm-scale pseudo-teepee occurs in the centre of the image (sample
1140	TZ 16-21; 107 m). (h, i) Closeup of graded lamina in (g) showing plastic deformation. The
1141	top of the lamina shows an erosion surface with small rip-up clasts (arrow), overlain by a
1142	coarser layer.

1143

**Figure 5.** SEM images of dolomites in backscatter mode: (**a**) Overview showing layer enriched in celestine inclusions (bright areas) in dolomite (Sample TZ14-9d; 95 m); (**b**) Celestine inclusion with barite in the centre (same sample as in a); (**c**) Barite crystals in dolomicrite (sample TZ14-4; 65 m).

1148

Figure 6. SEM images of dolomites in backscatter mode showing different types of crystal
shape: (a) Spheroidal growth of dolomite (darker areas) in clay layers (brighter areas; sample
TZ14-9d; 95 m). (b) Closeup of a. (c) Dolomite crystals showing a porous interior domain but
homogeneous syntaxial cement rims (sample TZ14-12; 90 m). (d) Similar as in (c; sample
TZ14-9d; 95 m).

1154

Figure 7. X-ray diffraction patterns: (a) Bulk analyses of homogeneous dolomite (Samples
TZ14-1, TZ14-7, and TZ14-9); main peaks and ordering peaks are labelled with (hkl) indices.
(b-d) Clay mineral separates of samples TZ14-1, TZ14-7 and TZ14-9, air dried (N), saturated





1158	with ethylene glycol (EG), and heated to 550°C (T); d-values in Å. In the ethylene-glycol
1159	saturated sample TZ14-9 the illite-smectite mixed-layer is best seen. The arrow points at the
1160	expandable (smectite) part of the mixed-layer.
1161	
1162	Figure 8. (a) Carbon/oxygen isotope cross-plot. (b) Oxygen isotope values through the
1163	stratigraphic section.
1164	
1165	Figure 9. Element concentrations in sequentially extracted fractions of bulk dolomite and
1166	clay samples of the Travenanzes Fm.: (a) Ca vs. Mg; (b) Sr vs. K.
1167	
1168	Figure 10. Comparison of Sr-isotopes in dolomites of the Travenanzes Fm. with Carnian
1169	seawater curve (Korte et al., 2003). The 2-sigma uncertainties are smaller than the symbol
1170	size.
1171	
1172	Figure 11. Sr-isotope values from dolomites of different modern and ancient environments:
1172 1173	Figure 11. Sr-isotope values from dolomites of different modern and ancient environments: Travenanzes Fm. in the Dolomites, Southern Alps; Germanic Keuper (Weser Formation and
1172 1173 1174	<b>Figure 11.</b> Sr-isotope values from dolomites of different modern and ancient environments: Travenanzes Fm. in the Dolomites, Southern Alps; Germanic Keuper (Weser Formation and Arnstadt Formation); Coorong Lagoon; Deep Springs Lake. <sup>87</sup> Sr/ <sup>86</sup> Sr ratios of modern
1172 1173 1174 1175	<b>Figure 11.</b> Sr-isotope values from dolomites of different modern and ancient environments: Travenanzes Fm. in the Dolomites, Southern Alps; Germanic Keuper (Weser Formation and Arnstadt Formation); Coorong Lagoon; Deep Springs Lake. <sup>87</sup> Sr/ <sup>86</sup> Sr ratios of modern seawater are from DePaolo and Ingram (1985).
1172 1173 1174 1175 1176	<b>Figure 11.</b> Sr-isotope values from dolomites of different modern and ancient environments: Travenanzes Fm. in the Dolomites, Southern Alps; Germanic Keuper (Weser Formation and Arnstadt Formation); Coorong Lagoon; Deep Springs Lake. <sup>87</sup> Sr/ <sup>86</sup> Sr ratios of modern seawater are from DePaolo and Ingram (1985).
1172 1173 1174 1175 1176 1177	Figure 11. Sr-isotope values from dolomites of different modern and ancient environments: Travenanzes Fm. in the Dolomites, Southern Alps; Germanic Keuper (Weser Formation and Arnstadt Formation); Coorong Lagoon; Deep Springs Lake. <sup>87</sup> Sr/ <sup>86</sup> Sr ratios of modern seawater are from DePaolo and Ingram (1985). TABLES
1172 1173 1174 1175 1176 1177 1178	<ul> <li>Figure 11. Sr-isotope values from dolomites of different modern and ancient environments:</li> <li>Travenanzes Fm. in the Dolomites, Southern Alps; Germanic Keuper (Weser Formation and Arnstadt Formation); Coorong Lagoon; Deep Springs Lake. <sup>87</sup>Sr/<sup>86</sup>Sr ratios of modern seawater are from DePaolo and Ingram (1985).</li> <li>TABLES</li> <li>Table 1. Compilation of sedimentary structures from thin section analysis of dolomites from</li> </ul>
1172 1173 1174 1175 1176 1177 1178 1179	<ul> <li>Figure 11. Sr-isotope values from dolomites of different modern and ancient environments:</li> <li>Travenanzes Fm. in the Dolomites, Southern Alps; Germanic Keuper (Weser Formation and Arnstadt Formation); Coorong Lagoon; Deep Springs Lake. <sup>87</sup>Sr/<sup>86</sup>Sr ratios of modern seawater are from DePaolo and Ingram (1985).</li> <li>TABLES</li> <li>Table 1. Compilation of sedimentary structures from thin section analysis of dolomites from the Travenanzes Fm. at the Dibona section.</li> </ul>
1172 1173 1174 1175 1176 1177 1178 1179 1180	<ul> <li>Figure 11. Sr-isotope values from dolomites of different modern and ancient environments: Travenanzes Fm. in the Dolomites, Southern Alps; Germanic Keuper (Weser Formation and Arnstadt Formation); Coorong Lagoon; Deep Springs Lake. <sup>87</sup>Sr/<sup>86</sup>Sr ratios of modern seawater are from DePaolo and Ingram (1985).</li> <li>TABLES</li> <li>Table 1. Compilation of sedimentary structures from thin section analysis of dolomites from the Travenanzes Fm. at the Dibona section.</li> </ul>
1172 1173 1174 1175 1176 1177 1178 1179 1180 1181	<ul> <li>Figure 11. Sr-isotope values from dolomites of different modern and ancient environments:</li> <li>Travenanzes Fm. in the Dolomites, Southern Alps; Germanic Keuper (Weser Formation and Arnstadt Formation); Coorong Lagoon; Deep Springs Lake. <sup>87</sup>Sr/<sup>86</sup>Sr ratios of modern seawater are from DePaolo and Ingram (1985).</li> <li>TABLES</li> <li>Table 1. Compilation of sedimentary structures from thin section analysis of dolomites from the Travenanzes Fm. at the Dibona section.</li> <li>Table 2. Relative abundances and ordering parameters of dolomites from the Travenanzes</li> </ul>
1172 1173 1174 1175 1176 1177 1178 1179 1180 1181 1182	<ul> <li>Figure 11. Sr-isotope values from dolomites of different modern and ancient environments:</li> <li>Travenanzes Fm. in the Dolomites, Southern Alps; Germanic Keuper (Weser Formation and Arnstadt Formation); Coorong Lagoon; Deep Springs Lake. <sup>87</sup>Sr/<sup>86</sup>Sr ratios of modern seawater are from DePaolo and Ingram (1985).</li> <li>TABLES</li> <li>Table 1. Compilation of sedimentary structures from thin section analysis of dolomites from the Travenanzes Fm. at the Dibona section.</li> <li>Table 2. Relative abundances and ordering parameters of dolomites from the Travenanzes Formation. Relative abundances were estimated based on the 104 peak height. The</li> </ul>





# Sr-isotopes in Carnian primary dolomite

1184	of Lumsden (1979). The structural ordering was calculated from the ratio of the 015 ordering
1185	peak to the 110 peak according to Füchtbauer and Goldschmidt (1966).
1186	
1187	Table 3. Total inorganic and organic carbon (TIC, TOC) contents of clay samples from the
1188	Travenanzes Formation.
1189	
1190	Table 4. Carbon and oxygen isotope values of different types of dolomite from the
1191	Travenanzes Formation.
1192	
1193	Table 5. Element concentrations of leacheates from dolomites and clays used for Sr-isotope
1194	analysis.
1195	
1196	Table 6. Compiled <sup>87</sup> Sr/ <sup>86</sup> Sr ratios of sequentially leached dolomites from different locations,

1197 clays and test minerals using different extraction solutions.











Figure 1



















Figure 4









Figure 4 continued



















Figure 7













Figure 9







Figure 10







Figure 11





Macroscopic Description	Height	Sam	ples		Matrix				Alloche	sme			Sec	imentary	structures		Porosi	λ <sub>μ</sub>	Deforms	tion	SMF**
		2014	2016	Aphano- topic	Micro- spar	Cavity- filling	Undeform. mud clasts*	Deformed mud clasts p	Flat Pack ebbles peloi	ids Ooid	s Quartz clasts	Bioclasts	Lamination	Graded Bedding	Pseudo- Teepee	Erosion F surfaces	Forosity p	Moldic 3	Soft sediment deformation o	Brittle	
dolomite with pyrite	120.0		TZ16-22	+	+	+	ŧ	+	+	•	•		+			+	+	+	+	‡	25
laminated dolomite/clay	111.0 1	TZ14-11	TZ16-20	‡	+	+	+	+I	++	'	•		‡	+	+	+I			+	‡	25
laminated dolomite	107.0	TZ14-10 7	Z16-21/St-3	+	+	+	+	+I	+	'	•		‡	+	+	‡	+		+	+	25
laminite	107.0		TZ16-17	‡	+	•	+	+	+	'	•	+	+I	+I		•	+	‡	+	+	25
dolomite nodule	105.0		TZ16-St-2	‡	+		+	+	' +I	'	•		•			,		,	+	+	diag.
homogeneous dolomite	104.0		TZ16-St-1	‡	+	+I	+	+I	+	'	•							,	+	+	23
nodular dolomite	100.01	TZ14-13		‡	+		+	+I		'	•		•						+I	+	diag.
dolomite nodule	96.0		TZ16-15	‡	+I	+	‡	+I	+1	'	•		•						‡	‡	diag.
laminated dolomite	95.0	TZ14-9		+		+	+	+	++	'	•		‡	+	+	+	+	,	+	+	25
porous dolomite	B9.0	TZ14-12		+	+I		+	+I	, ,	'	•	Forams Biocl.					+	‡	+	+	23
nodular bed	80.0		TZ16-13	‡	+	+	+	+I		'	•	(+)				,	+I	+	+		diag.
palaeosol, nodule	79.0		TZ16-12	+	+I	+I	+	+I	'	'	•		•					+	‡	‡	diag.
sandy dolomite (congl.)	75.0	TZ14-5	TZ16-11	‡	+I	+I	‡	+I	' ‡	'	+	Ostracods (+)	•			,	+I	+I			23
sandstone	74.0		TZ16-10	+	+I		‡	,	'	'	+		•	•	•	•		•	•		25
brittle porous dolomite	65.0	TZ14-4		+		+	+I		+	+	•	Forams +	-	+			+	+	+	+	15
porous dolomite	43.0		TZ 16-7	‡	+I	+	+I	+I		'	•	Ostracods ±	•				+I	+	‡	+	23
nodules of dolomite	35.0	TZ14-3		‡	+			+I	•	'	•		•						+	+	diag.
dolomite nodule	35.0	TZ14-2		+	+I	•		+I	' '	'	•		•	•		•		•	+	+	diag.
arenite	33.5		TZ16-8	+	+I		+		Ŧ	' +	‡			+					+	+	Sst.
homogeneous dolomite	33.0	TZ14-1		‡	+I		+	+	+	'	H		+I	+I	•	•		•	+	+	23
laminated dolomite	31.5		TZ16-2	+	•	•	+			'	‡		+	+	•	+	+	•	+I	+I	Sst.
palaeosol, dolomit	30.1		TZ16-3	‡		+I	+	+I		'	•			•					+	+	diag.
red mottled dolomite	26.0	TZ14-7				•	+I	+I		'	•		•			+I			+I	+I	23
dolomite with clay	21.0	TZ14-8		‡	+I	•	H	H		'	•		+I	•	•	•	•	•	•	•	23
homogeneous dolomite	4.0	TZ14-6		‡	+	+I	+	+	+	•	•	Forams +	+	+	+	+		+	+	+I	25
	- not pres	ent ≞	rare		+ common		++ very abund	ant (+	-) putative								1 7	* Nodules	are most likely a ssociated to a	diagenetic ar a microfacies	d can
	* Needs to	be further (	ubdivided into	peloids, in	ntraclasts, fl.	at pebbles an	d clast of brittle	deformation													
	Ĭ	omodeneor	us dolomite			aminated dol	omite	Z	odular dolomit	a		Oolithic dolomite				S	andstone				





Sample	Depth	d(A°)	Ca/(Ca+Mg)	015/110
	(m)		(%)	
TZ14-1	33.0	2.88944	51.1	0.44
TZ14-7	43.0	2.88871	50.9	0.41
TZ14-9	95.0	2.88633	50.1	0.46





Sample	TC (wt%)	TOC (wt%)	TIC (wt%)
TZ16-1	0.06	0.05	0.02
TZ16-19B	0.12	0.11	0.02
TZ16-5	0.16	0.05	0.12
TZ16-19A	0.34	0.10	0.25
TZ16-14	0.42	0.16	0.27
TZ16-18	0.50	0.07	0.43
TZ16-16	0.51	0.05	0.46





Sample	Depth	δ¹³C	δ18Ο	Туре	Description				
	(m)	(‰ VPDB)	(‰ VPDB)						
IZ14-1	33	1.04	-0.76	homogeneous	with siliciclastis				
TZ14-3	35	-1.58	-1.11	nodule	with barite				
TZ14-4	65	-0.15	-0.22	peloidal	with apatite				
TZ14-6	4	2.90	-1.22	homogeneous	with siderite and pyrite				
TZ14-8	21	3.73	-0.84	homogeneous	with clay, apatite and Fe-oxide				
TZ14-9	95	-1.01	0.21	laminated	with celestine and barite				
TZ14-10b	107	-1.05	0.26	laminated	with apatite and pyrite				
TZ14-11	111	0.79	0.64	homogeneous	homog. Lamina with clay and pyrite				
TZ14-12	89	-0.15	0.36	peloidal	with megalodont and Ti-oxides				
TZ14-13	100	-3.38	0.23	nodule	palaeosol with Fe-oxide				
TZ16-St1	104	-2.74	0.38	homogeneous	mud clast top				
	104	-2.71	0.34	homogeneous	matrix				
TZ16-St2	105	-3.08	0.12	nodule	matrix top				
	105	-2.86	0.22	nodule	matrix bottom				
TZ16-7	43	-2.91	-0.36	Rauhwacke	matrix top				
	43	-2.11	-0.67	Rauhwacke	matrix bottom				
TZ16-13	80	-2.03	0.15	nodule	matrix top				
	80	-1.94	0.01	nodule	matrix bottom				
TZ16-21	107	-0.86	0.18	laminated	graded lamina				
	107	-1.09	0.17	laminated	ligh lamina				
	107	-0.88	0.23	laminated	dark lamina				
TZ16-22	120	1.72	0.45	homogeneous	mud clast				
	120	1.22	0.15	homogeneous	lamination				
	120	2.97	0.54	homogeneous	homogeneous part				
TZ16-St3	107	-1.07	0.34	laminated	dark layer, lense				
	107	-1.00	0.07	laminated	dark layer bottom				
	107	-1.18	0.28	laminated	dark layer top				
	107	-1.12	0.06	laminated	light layer top				





Table 5
---------

Sample Element	Element		0.1 N acetic a	cid fraction		1 N a	1 N HCl fraction			
		µmol/g	µmol/g	µmol/g	µmol/g	µmol/g	µmol/g	µmol/g	µmol/g	µmol/g
Bulk dold	omite samples									
		TZ14-1	TZ14-7	TZ14-9	crystal	TZ14-1	TZ14-7	TZ14-9		
		0.098 g	0.127 g	0.099 g	0.094 g	0.098 g	0.127 g	0.099 g		
	AI	6.58	3.17	11.57	3.04	4.51	8.17	5.97		
	Ca (mmol/g)	1.68	2.33	1.88	2.50	2.87	2.71	2.75		
	Fe	4.97	3.53	10.67	34.27	2.04	9.15	5.02		
	К	3.32	9.71	5.26	0.93	10.31	4.65	13.51		
	Mg (mmol/g)	1.61	2.13	1.77	2.34	2.64	2.48	2.50		
	Mn	5.96	3.57	7.68	15.24	10.84	3.72	10.67		
	Na	12.78	18.98	17.32	1.85	17.35	20.12	23.30		
	Р	1.50	n.d.	0.98	n.d.	0.20	1.45	n.d.		
	Ti	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
	Ba	0.50	0.03	0.48	n.d.	1.75	0.02	1.03		
	Sr	0.38	1.00	1.16	0.13	0.79	0.57	34.91		
	Rb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
Clay sam	ples									
		TZ16-1	TZ16-19B			TZ16-1	TZ16-19B		TZ16-1	TZ16-19B
		0.038 g	0.030 g			0.038 g	0.030 g		0.038 g	0.030 g
	AI	2.18	4.52			1.54	4.01		39.86	33.62
	Ca	19.14	11.62			8.48	4.34		0.71	0.60
	Fe	0.72	1.79			0.83	2.25		75.59	11.56
	к	4.97	9.02			2.77	3.69		11.69	12.61
	Mg	8.05	13.76			4.46	6.07		24.62	18.75
	Mn	n.d.	n.d.			n.d.	n.d.		n.d.	n.d
	Na	0.355	0.470			0.305	0.389		0.531	0.828
	Р	6.89	1.08			0.67	n.d.		n.d.	n.d
	Ti	n.d.	n.d.			n.d.	n.d.		1.305	0.194
	Ва	n.d.	n.d.			n.d.	n.d.		0.022	n.d
	Sr	0.417	0.047			0.187	0.018		0.017	0.005
	Rb	n.d.	n.d.			n.d.	n.d.		n.d.	n.d





Table 6. Sr-isoto	opes													
Sample	Section	Description	Seq.	Weight	Reagent	Amount	Extr. T	Extr.	Shake	r Washing	Run no.	#Sr/#Sr	2σ (10°)	Aliquot for
	(m)		extr.	(mg)		(ml)	(°C)	time	y/n	(before step)				conc.
NBS987 NBS988		Standard solution (500 ppm) Standard solution (500 ppm)		500 ng 500 ng							(n = 40) (n = 9)	0.710272 0.710268	4 6	
Test minerals Series 1 (sequer	ntial extrac	tion)												
Celestine				2.34	1M NaCl 0.1N AcOH	2 ml	20 20	12 h	n	1M NaCl 2M NaCl 1M KCl H O	6052	0.708037	5	
Dolomite				9.88	0.1N AcOH	2 mi	20	12 h		0.1N AcOH	6110	0.700007	11	
Mixture		Barite 4.5 mg. Celestine	sea	49.31	1M NaCi	2 ml	20	12 h	n	0.1N AcOH 1M NaCi	6053	0.708038	3	
Mixture		8.91 mg; Dolomite 35.9 mg	seq.		0.1N AcOH	2 ml	20	12 h	n	3M NaCL 1M KCL H.O.	6108	0.709501	40	
								12 h		0.1N AcOH				
Series 2				0.00		0						0 7000 45		
Celestine				4.60	0.1N AcOH	2 mi 2 ml	20	2 n 4 h	n	- 12h 1M NaCl	6121	0.708045	4	
Barite			sea	36.94	6N HCI 6N HCI	2 ml 2 ml	40 40	12 h 12 h	n	-	6152 6155	0.707610	5	
Dolomite		Berlinde		17.37	0.1N AcOH	5 ml	40	12 h	n	-	6068	0.710831	7	
Dolomite		Replicate		3.41	0.1N ACOH	2 mi	40	12 N	n	-	6114	0.710557	11	
Travenanzes Fn Bulk samples se	n. quential ex	tractions, Series 1												
TZ14-1 TZ14-1	33 m 33 m	homogeneous dolomite	seq.	12.35	1M NaCl 0 1N AcOH	2 ml 3 x 2 ml	20 20	12 h 4h 12h 4h	n v	- 1M NaCL H O 3 3M	6112 6169	0.708125	12 4	
T714-1	22 m	homogonoous dolomito	600			2 ml	20	96 h	,	KCI. H.O	6179	0 715417	250	
1214-1	35 11	nomogeneous dolonne			0.111 ACOT	2 110	20	3011	y		01/5	0.713417	230	
TZ14-9 TZ14-9	95 m 95 m	laminated dolomite laminated dolomite	seq. seq.	13.50	1M NaCl 0.1N AcOH	2 ml 3 x 2 ml	20 20	12 h 4h, 12h, 4h	n y	- 1M NaCl, H₂O, 3.3M	6113 6171	0.707880 0.707817	4 5	
TZ14-9	95 m	laminated dolomite	seq.		0.1N AcOH	2 ml	20	36 h	у	- KCI H.O	6174	0.719226	455	
Mixture		Residue from test mineral	seq.		0.1N AcOH	3 × 2 ml	20	4h, 12h, 4h	v	1M NaCl. H.O. 3.3M	6172	0.709812	5	
Mixture		series 1 Residue from test mineral	seq.		0.1N AcOH	2 ml	20	36 h	ý	KCI H.O	6176	0.709900	4	
		series 1												
TZ14-1	33 m	homogeneous dolomite		42.76	0.1N AcOH	2 ml	20	4 h	n		6130	0.707894	4	
TZ14-9	95 m	laminated dolomite		17.69	0.1N AcOH	2 ml	20	4 h	n		6131	0.707872	5	
Bulk complete co	guartial as	tractions Spring 2												
TZ14-1	33 m	homogeneous dolomite		93.91	1M NaCl	10 ml	20	12 h	У		6182	0.708096	5	
TZ14-1 TZ14-1	33 m 33 m	homogeneous dolomite homogeneous dolomite	seq. seq.	98.28	0.1N AcOH 1N AcOH	10 ml 10 ml	20 20	12 h 12 h	y y	-	6183 6205	0.707812 0.707670	4 5	yes yes
TZ14-1	33 m	homogeneous dolomite		50.00	6N HCI	5 ml	20	12 h	n	10h 1N CH,COOH	6445	0.710403	6	
TZ14-7	26 m	mottled dolomite		90.64	1M NaCl	10 ml	20	12 h	У		6179	0.707883	4	
TZ14-7 TZ14-7	26 m 26 m	mottled dolomite mottled dolomite	seq. seq.	127.52	0.1N AcOH 1N AcOH	10 ml 10 ml	20 20	12 h 12 h	y y	-	6178 6207	0.707801 0.707719	4	yes yes
TZ14-7	26 m	mottled dolomite		50.00	6N HCI	5 ml	20	12 h	n	10h 1N CH <sub>2</sub> COOH	6449	0.730453	5	
TZ14-9	95 m	laminated dolomite		97.82	1M NaCl	10 ml	20	12 h	у		6187	0.707869	3	
TZ14-9 TZ14-9	95 m 95 m	laminated dolomite	seq.	98.76	0.1N AcOH 1N AcOH	10 ml 10 ml	20 20	12 h 12 h	У	-	6185 6206	0.707862	3	yes ves
TZ14-9	95 m	laminated dolomite		50.00	6N HCI	5 ml	20	12 h	'n	10h 1N CH <sub>2</sub> COOH	6447	0.708464	4	,
Dolomite (sing	le crystal)	control		116.65	1M NaCl	10 ml	20	12 h	у	-	6184	0.708401	40	
Dolomite (sing Dolomite (sing	le crystal) le crystal)	control	seq. seq.	94.12	0.1N AcOH 1N AcOH	10 ml 10 ml	20 20	12 h 12 h	y y	-	6180 6208	0.707735	6	yes yes
Micro drill compl	100													
TZ14-3	35 m	dolomite nodule			0.1N AcOH	2 ml	20	24 h	n	H <sub>2</sub> O, 5min 0.1N AcOH	6548	0.707976	4	
TZ14-4 TZ14-6	65 m 4 m	peloidal dolomite homogeneous dolomite			0.1N AcOH 0.1N AcOH	2 ml 2 ml	20 20	24 h 24 h	n n	H <sub>2</sub> O, 5min 0.1N AcOH H.O. 5min 0.1N AcOH	6549 6550	0.707711 0.707830	4	
TZ14-8	21 m	dolomite with clay		-	0.1N AcOH	2 ml	20	24 h	n	H <sub>2</sub> O, 5min 0.1N AcOH	6551	0.707821	4	
TZ14-10b TZ14-11	107 m 111 m	laminated dolomite			0.1N ACOH 0.1N ACOH	2 ml 2 ml	20 20	24 h 24 h	n	H <sub>2</sub> O, 5min 0.1N AcOH H <sub>2</sub> O, 5min 0.1N AcOH	6554 6553	0.707886	4	
TZ14-12	89 m	peloidal dolomite		-	0.1N AcOH	2 ml	20	24 h	n	H <sub>2</sub> O, 5min 0.1N AcOH	6555	0.707848	4	
1214-13	100 111	dolonnite with palaeosol		-	0.111 ACOT	2 110	20	2411		H <sub>2</sub> O, Smirro. HV ACOT	0000	0.707072	4	
Micro-drilled seq TZ14-1	uential ext 33 m	ractions homogeneous dolomite	seq.		0.1N AcOH	2 ml	20	24 h	n	H <sub>2</sub> 0, 5min 0.1N AcOH	6411	0.707672	3	
TZ14-1	33 m	homogeneous dolomite	seq.		1N AcOH		20	24 h	n	H <sub>i</sub> 0, 5min 0.1N AcOH	6448	0.708300	23	
TZ14-7	26 m	mottled dolomite	seq.		0.1N AcOH	2 ml	20	24 h	n	H₂0, 5min 0.1N AcOH	6479	0.707775	6	
TZ14-7	26 m	mottled dolomite	seq.	-	1N AcOH		20	24 h	n	H <sub>2</sub> 0, 5min 0.1N AcOH	6444	0.708502	22	
TZ14-7	26 m	clay layer	seq.		0.1N AcOH		20	24 h	n	H,0, 5min 0.1N AcOH	6410	0.707742	4	
1214-7	2011	Cidy layer	seq.		IN ACOH		20	2411		H <sub>1</sub> 0, Smirt 0. TN ACOH	0440	0.708467	2	
TZ14-9 TZ14-9	95 m 95 m	laminated dolomite laminated dolomite	seq. seq.	2	0.1N AcOH 1N AcOH	2 ml	20 20	24 h 24 h	n n	H <sub>2</sub> 0, 5min 0.1N AcOH H <sub>2</sub> 0, 5min 0.1N AcOH	6412 6443	0.707813 0.708281	149 56	
Clav samples														
TZ16-1	32 m	red (green) clay	seq.	38.30	0.1N AcOH	2 ml	20	12 h	n	2h 0.1N AcOH	6557	0.707771	4	yes
TZ16-1 TZ16-1	32 m 32 m	red (green) clay red (green) clay	seq. seq.		6N HCI	2 mi 2 ml	20	12 h	n	4h 6N HCI	6559	0.707768	4	yes yes
TZ16-19B	110 m	dark grev clav	sea	29 74	0 1N AcOH	2 ml	20	12 h	n	2h 0 1N AcOH	6560	0 708299	8	Ves
TZ16-19B	110 m	dark grey clay	seq.	-	1N AcOH	2 ml	20	12 h	n	2h 1N AcOH	6561	0.708582	8	yes
I∠16-19B	110 m	dark grey clay	seq.		6N HCI	2 ml	20	12 h	n	4n 6N HCI	6552	0.733910	24	yes
Germanic Keup Lehr	er	micro-drilled			0.1N AcOH	2 ml	20	24 h	n	H.0. 5min 0 1N AcOH	6545	0.709303	4	
Keu 1-2 B		micro-drilled		-	0.1N ACOH	2 ml	20	24 h	n	H <sub>2</sub> 0, 5min 0.1N AcOH	6546	0.709805	6	
Deep Springs L	ake													
DS11-3, 16.5	16.5 cm	dried mud	seq.	91.17	0.1N AcOH	10 ml	20	5 min	n	H,O H,O	6363 6363	0.713207	4 4	
DS11-3, 52.5	52.5 cm	dried mud	<u>.</u>	62.19	0.1N ACOH	10 ml	20	10 h	n	H <sub>i</sub> O	6343	0.713035	4	
Milne Lake (Cod	orong)													
CM01-3 CM01-3	30 cm	dried mud, ground	seq.	47.94	0.1N AcOH	10 ml	20	5 min	n	H,O H,O	6340 6340	0.709251	4	
CM01-9	90 cm	dried mud, ground	<u></u>	52.47	0.1N ACOH	10 ml	20	10 h	n	H,O	6341	0.709272	4	