Dolomitization by hypersaline reflux into dense groundwaters as revealed by vertical trends in Sr and O Isotopes: Upper Muschelkalk, Switzerland

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Abstract

The Trigonodus Dolomit is the dolomitized portion of the homoclinal ramp sediments of the Middle Triassic Upper Muschelkalk in the SE Central European Basin. Various dolomitizing mechanisms, followed by recrystallization, have been previously invoked to explain the low $\delta^{18}\text{O}$, high $^{87}\text{Sr}/^{86}\text{Sr}$, extensive spatial distribution and early nature of the replacive matrix dolomites. This study re-evaluates the origin, timing and characteristics of the dolomitizing fluids by examining petrographic and isotopic trends in the Trigonodus Dolomit at 11 boreholes in northern Switzerland. In each borehole the *ca* 30 m thick unit displays the same vertical trends with increasing depth: crystal size increase, change from anhedral to euhedral textures, UV-fluorescence decrease, $\delta^{18}\text{O}_{\text{VPDB}}$ decrease from -1‰ at the top to -6.7‰ at the base and an $^{87}\text{Sr}/^{86}\text{Sr}$ increase from 0.7080 at the top to 0.7117 at the base. Thus, dolomites at the top of the unit record isotopic values similar to Middle Triassic sea water ($\delta^{18}\text{O}_{\text{VSMOW}} = 0\text{‰}$; $^{87}\text{Sr}/^{86}\text{Sr} = 0.70775$) while dolomites at the base record values similar to meteoric groundwaters from the nearby Vindelician High ($\delta^{18}\text{O}_{\text{VSMOW}} = -4\text{‰}$; $^{87}\text{Sr}/^{86}\text{Sr} = >0.712$). According to water–rock interaction modelling, a single dolomitizing or recrystallizing fluid cannot have produced the observed isotopic trends. Instead, the combined isotopic, geochemical and petrographic data can be explained by dolomitization via seepage-reflux of hypersaline brines into dense, horizontally-advecting groundwaters that already had negative $\delta^{18}\text{O}$ and high $^{87}\text{Sr}/^{86}\text{Sr}$ values. Evidence for the early groundwaters is found in meteoric calcite cements that preceded dolomitization and in fully recrystallized dolomites with isotopic characteristics identical to the groundwaters

following matrix dolomitization. This study demonstrates that early groundwaters can play a decisive role in the formation and recrystallization of massive dolomites and that the isotopic and textural signatures of pre-existing groundwaters can be preserved during seepage-reflux dolomitization in low-angle carbonate ramps.

1 Introduction

Dolomites of the Middle Triassic Upper Muschelkalk are a major stratigraphic unit of central Europe with an areal extent of more than 100 000 km² across Switzerland, Germany and France. Locally they serve as shallow freshwater aquifers and in their deeper realms their saline aquifer properties show potential for CO₂ storage and geothermal energy (Chevalier et al., 2010). The major replacive dolomite horizon in the Upper Muschelkalk, the Trigonodus Dolomit, is no exception to the “dolomite problem” (e.g. Zenger et al., 1980; Hardie, 1987; Machel, 2004) and its enigmatic genesis has been investigated since the 1980s. Based on the spatial distribution of the Trigonodus Dolomit, Alesi (1984) suggested that replacive dolomitization occurred according to the evaporative pumping model of Hsü & Siegenthaler (1969). Iron-rich matrix dolomites with light oxygen isotopes, associated with evaporative textures, were attributed by Schauer and Aigner (1997) to a three-stage dolomitization history beginning with evaporative dolomitization followed by two stages of burial dolomitization. Zeeh & Geng (2001) discovered notably radiogenic ratios of strontium isotopes in matrix dolomites at multiple boreholes across Germany and proposed early evaporative dolomitization, followed by late-stage cementation by saddle dolomites during the rifting of the Rhine graben. Koehrer et al. (2010) expanded on the above-mentioned studies by adding a telogenetic stage, which leached out much of the late-stage saddle dolomites. Turpin et al. (2012) attributed the dolomites to burial dolomitization. Additionally, many authors have ascribed the negative $\delta^{18}\text{O}$ and radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of matrix dolomites to recrystallization during burial or to meteoric fluids (Schauer and Aigner, 1997; Zeeh and Geng, 2001; Turpin et al., 2012). In summary, a wide variety of dolomitizing fluids and settings have been invoked to explain the occurrence of dolomite in the Upper Muschelkalk.

The above variety of models is in part due to the selectivity of methods used to study the dolomitization events. Each method yields evidence which, examined on its own, may exclude some types of dolomitizing fluid but remains consistent with several others. Therefore, an opportune approach is to build on the previous works and conduct a comprehensive study of the Trigonodus Dolomit, combining variations in the extent and thickness of the dolomite, its geochemistry, stable and strontium isotopes, and petrographic observations. Integration of these variables can account for the perceived differences in dolomite extent, thickness and geochemistry; and can resolve the confusion over the cause of the Upper Muschelkalk dolomitization.

Adopting the above approach, this paper sets out to uncover the source of the dolomitizing and recrystallizing fluid(s), their geochemical properties and the explanation behind the huge spatial

extent of dolomite in the Central European Basin (CEB), with emphasis on the Swiss Upper Muschelkalk and its spatial variations. It is recognized that trace element partitioning and isotopic fractionation between water and dolomite are controlled by a wide range of factors including temperature, water/rock ratios, isotopic and trace element compositions of the host fluids and precursor minerals, stoichiometry, precipitation rates and potentially by modifications of these signatures by later diagenesis (Land, 1980; Pingitore, 1982; Hardie, 1987; Banner & Hanson, 1990; Vahrenkamp & Swart, 1990). Therefore, in this study geochemical and petrographical data are carefully juxtaposed with rock/water interaction models and multiple petrographic methods to identify the most likely dolomitizing process.

2 Palaeogeography and geology

During the Middle Triassic the CEB was located between 15° and 30° N in a semi-arid environment with monsoonal seasons and strong winter storms (Aigner, 1985; Parrish, 1993; Stampfli & Borel, 2002). The basin was separated from the Tethys Ocean by the Vindelician High to the east, the London-Brabant Massif to the west, and by three tectonically controlled gates, which periodically allowed Tethys marine waters into the basin (Fig. 3.1A; Ziegler, 1990). Northern Switzerland lay offshore from the Vindelician High in the southern CEB near the Burgundy Gate (Fig. 3.1B). During the late Illyrian, the opening of the Burgundy Gate resulted in the development of an extensive homoclinal carbonate ramp in the semi-enclosed epeiric sea within the CEB (Kozur, 1974). These sediments constitute the Upper Muschelkalk unit (Hagdorn & Nitsch, 2009).

Figure 3.1. (A) Palaeogeographic reconstruction of the Central European Basin (CEB) during the Anisian/Ladinian (modified from Ziegler, 1990). Arrows show the periodic movement of Tethys sea waters into the German Basin. RM denotes Rhenish Massif. (B) Location of examined and sampled boreholes within northern Switzerland.

Epoch	Age	Disler (1914)		DSK (2002)	Pietsch et al. (2016)	Lithology	Thickness in Switzerland (m)
Middle Triassic	Ladinian	Gipskeuper	Middle Keuper	Grabfeld Fm.	Bänkerjoch Fm.		>70
		Lettenkohle	Low. Keuper	Erfurt Fm.	Asp Member		~10
	Anisian	Trigonodus-dolomit	Upper Muschelkalk	Rottweil Formation	Stamberg Mb.		~28
		Haupt-muschelkalk		Meißen Formation	Liedertswil Mb.		~40
				Trochitenkalk Formation	Kienberg Mb.		
		Anhydrit-dolomit	Middle Muschelkalk	Diemel Formation	Leutschenberg Mb.		
		Sulfat-schichten		Heilbronn Formation	Zelingen Fm.		~15
							~40

	Dolomite		Limestone		Marl		Sulphate
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Figure 3.2. Stratigraphy of Middle Triassic rocks of the Upper Muschelkalk (modified from Adams and Diamond, 2017) in Switzerland (Disler, 1914; Jordan, 2016; Pietsch et al., 2016) and Germany (DSK, 2002, where DSK denotes Deutsche Stratigraphische Kommission, 2002). Note the erosional contact between the Lettenkohle and Trigonodus Dolomit. The classification of Disler (1914) is used throughout this publication.

The Upper Muschelkalk is divided into a retrogradational transgressive system tract (TST), which initiated directly after the deposition of Middle Muschelkalk evaporites, followed by a progradational highstand systems tract (HST), which concluded at the base of the Keuper Lettenkohle (Erfurt Formation) (Aigner & Bachmann, 1992). Both systems tracts are represented by coarsening-upwards, cyclical stacking-patterns of tempestites, shelly/oolitic shoals, lagoonal and supratidal sediments (Aigner, 1985). Based on these small-scale cyclical events, the Upper Muschelkalk sequence represents an overall basin-wide third-order, transgressive–regressive event (Aigner & Bachmann, 1992).

The Upper Muschelkalk reaches over 70 m in thickness at the centre of the southern CEB and is divided into two lithologically distinct units: the fully dolomitized Trigonodus Dolomit and the underlying, predominantly calcitic but dolomite-bearing Hauptmuschelkalk (Fig. 3.2). The base of the Trigonodus Dolomit is locally discordant to bedding and its thickness varies from < 10 m in southern Germany to > 35 m in northern Switzerland (Alesi, 1984). The Trigonodus Dolomit mostly represents the dolomitized back shoal sediments of the homoclinal ramp and is characterized by an increasing number of evaporite textures, including chicken wire anhydrites along with mud cracks and palaeosol facies towards the top of the unit (Schauer and Aigner, 1997) (Fig. 3.3A). Additionally, sediment shed from the two tectonic highs formed sandy shorelines at the top of the Upper Muschelkalk along the eastern and western margins of the epeiric sea (Aigner, 1982; Vecsei, 1998). Although sandy shorelines are marked across eastern Switzerland in palaeogeographic reconstructions (Fig. 3.1A), no sandstones have been observed yet in the Swiss Upper Muschelkalk, presumably due to the lack of borehole data in eastern Switzerland.

Figure 3.3. Common sulphate textures of the Trigonodus Dolomit and Lettenkohle. (A) Anhydrite crystal laths (bottom half of the image) are among the many common evaporite textures present at the top of the Trigonodus Dolomit (scale in m; Pfaffnau, 1546.48 m depth). (B) Lettenkohle dolomites in Switzerland often display chicken wire sulphate textures (Weiach, 814.48 m depth). (C) Lettenkohle evaporites displaying regular occurrences of sulphates (light grey) between clay-rich beds (dark grey; Weiach, 811.06 m depth).

At the conclusion of the third-order transgressive–regressive cycle of the Upper Muschelkalk, the basin was infilled from the north by brackish and coastal–plain–fluvial sediments of the Lettenkohle that had prograded up to 100 km into the basin from areas of non-deposition (Pöppelreiter & Aigner, 2008; Franz et al., 2013, 2015). The first occurrence of this transition is often marked by the Grenzbonebed, a condensed tempestite horizon at the base of the Keuper (Reif, 1982). The Lettenkohle sediments comprise up to 11 carbonate–shale–carbonate shallowing-upwards cycles that transition into overlying sabkha facies of the Middle Keuper (Pöppelreiter & Aigner, 2003; Franz et al., 2013, 2015). Within Switzerland, these cycles display interbedded sulphate bodies (Fig. 3.3B and C), which disappear northwards into central Germany where the Lettenkohle is characterized by increasing clay and siliciclastic contents (Franz et al., 2013). The Muschelkalk/Keuper transition is occasionally marked by unconformities in the form of incised valley-fills (Franz et al., 2013), by an angular unconformity above the Grenzbonebed and the Estherienschiefer (Wagner, 1913; Merki, 1961), and by disconformities at the tops of intra-basinal swells (Aigner & Bachmann, 1992). It remains unclear how much sediment was eroded at the contact between the Upper Muschelkalk and Keuper. Consequently, the original total thickness of the Upper Muschelkalk is unknown.

3 Samples and methods

Dolomite was examined in drill core from 11 boreholes drilled by Nagra (National Cooperative of the Disposal of Radioactive Waste), SEAG (Schweizerische Erdöl AG) and SBB (Swiss Federal Railways). The boreholes are all located in northern Switzerland (Fig. 3.1B). Samples from the drill cores were prepared and analysed at the University of Bern. More than 100 thin sections were stained to differentiate calcite from dolomite (Dickson, 1966). Spot analyses of carbonate major element compositions (Fe, Mg, Ca) from polished thin sections were obtained using a JEOL JXA-8100 electron microprobe (JEOL Ltd., Tokyo, Japan) with 15 kV accelerating voltage, 10 nA beam current and 10 µm beam diameter. These settings were used to minimize beam damage to the dolomite. The

same polished thin sections were imaged using a hot-cathode, cathodoluminescence (CL) microscope with 20 kV beam voltage, as described and designed by Ramseyer et al. (1989). All thin sections were imaged for fluorescence by UV reflected-light microscopy with an Olympus BX51 microscope coupled with an Olympus U-RFL-T mercury source (Olympus, Tokyo, Japan). Trace element analyses were performed by laser-ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) with a GeoLas Pro 2006 system (Coherent Inc., Santa Clara, CA, USA) referenced to the GSD-1G synthetic basalt standard at the University of Bern (Bern, Switzerland). Depth profiles were processed using SILLS, an LA-ICP-MS data reduction program (Guillong et al., 2006). Isochore maps were generated using data from four visually logged wells in Switzerland, 25 scientific and company reports, and 54 boreholes in France, accessed via the Guichet Hydrocarbures database of the Bureau Exploration-Production des Hydrocarbures (BEPH) (Table A3.1). Isochore maps were produced by a kriging interpolation algorithm from the R package ‘gstat’ (R Core Team, 2015). The thickness of the Upper Muschelkalk was taken as the distance between the top of the dolomite capping the Middle Muschelkalk (Anhydritdolomit der Anhydritgruppe) and the base of the thick Lettenkohle claystones. The thickness of the Trigonodus Dolomit was taken as the thickness of the continuous body of massive dolomite in the Upper Muschelkalk. The volumetric fraction of dolomite in the Upper Muschelkalk was taken as equivalent to the Trigonodus Dolomit thickness divided by the Upper Muschelkalk thickness. In some low-resolution logs, thicknesses could only be visually estimated, whereas other BEPH logs were avoided due to difficulties in identifying lithologies and calculating thicknesses. Additionally, some of the assembled boreholes appear to have been incorrectly logged. An example is the Lindau log in Switzerland, where according to Büchi et al. (1965) only 9.5 m of the Upper Muschelkalk is dolomitized. However, electron microprobe analyses and Raman spectroscopy of thin sections of the core revealed that > 37 m are fully dolomitized. Similar discrepancies cannot be ruled out in the BEPH logs used for boreholes that have not been examined directly.

Stable-isotope compositions of C and O were measured in duplicate on 150 µg of powder, drilled from thin section slabs or core. Only matrix dolomites were sampled and not the dolomite cements that are common to bioclastic horizons. Most samples are composed entirely of dolomite, so no acid separation of calcite was required. In cases where calcite was suspected in the matrix, the rock powders were reacted with 0.5 M acetic acid for 5 minutes. Then the mixture was rinsed with distilled water and dried. The samples were then verified by XRD with a CubiX³ diffractometer (Malvern Panalytical, Malvern, UK) to determine if any calcite remained. The aliquots were analysed for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in a Finnigan Delta V Advantage mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Isotope ratios in dolomite were corrected for phosphoric acid fractionation at 70 °C according to Rosenbaum & Sheppard (1986). This resulted in a correction of -1.206‰ on all dolomite $\delta^{18}\text{O}$ values. Isotope ratios in calcite were corrected on-line using a Carrara marble internal

standard. Oxygen and carbon isotopic compositions are reported in per mil Vienna Pee Dee Belemnite (VPDB).

For $^{87}\text{Sr}/^{86}\text{Sr}$ determinations, 35 carbonate and evaporite samples were dissolved in 7 M HNO_3 , centrifuged to remove organic material and analysed in a TRITON thermal ionization mass spectrometer (TIMS) (Thermo Fisher Scientific, Waltham, MA, USA). Strontium ratios were calibrated against the NIST SRM 987 standard ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710248 \pm 0.000029$ 2σ SD). Care was taken to select samples with low clay contents to avoid any strontium derived from detrital Rb (Banner, 1995).

Microthermometry of fluid inclusions was performed with a Linkam MSD-600 heating-cooling stage (Linkam Scientific Instruments, Tadworth, UK) mounted on an Olympus BX51 microscope (Olympus, Tokyo, Japan). The stage was calibrated against phase transitions in synthetic CO_2 – H_2O and H_2O inclusions, such that measurements below 0 °C are accurate to 0.1 °C.

4 Results

4.1 Petrography

4.1.1 *Trigonodus matrix dolomite*

Trigonodus matrix dolomites (TMD) constitute the entire Trigonodus Dolomit. No facies, structures or allochems escaped dolomitization. The TMD are finely to coarsely crystalline (on average 2 to 40 μm), matrix-replacive, fabric destructive, anhedral to euhedral dolomites (Adams and Diamond, 2017). At the top of the Trigonodus Dolomit the TMD are anhedral with crystal sizes around 2 μm (Fig. 3.4A). They gradually coarsen downwards, attaining a euhedral texture at its base with average crystal sizes *ca* 40 μm (Fig. 3.4B) and some crystals >100 μm . These downwards textural-trends are present in all boreholes regardless of their current depth. Crystal compaction via pressure-solution occurred in all boreholes (Fig. 3.4C) but is more prominent in deeper boreholes. Dolomite crystal rims are clear but the cores are rich in single-phase fluid inclusions ≤ 3 μm in diameter. The metastable absence of vapour bubbles is typical of fluid inclusions trapped below ~ 70 °C at depths below the vadose zone (Diamond, 2003). The occurrence of the inclusions in 3D clouds without planar arrays demonstrates that they are of primary origin and hence they represent the parent dolomitizing fluid from which the crystal cores precipitated.

Figure 3.4. Cathodoluminescence (CL) and UV-fluorescence images of Trigonodus Matrix Dolomites (TMD). (A) UV-fluorescence image of TMD at the top of the Trigonodus Dolomit (TD) displaying few dolomite cements, anhedral crystals and bright fluorescence. Intercrystalline porosity is shown in blue (Schlattingen, 1127.79 m). (B) UV-fluorescence image of the TMD at the base of the Trigonodus Dolomit in the same borehole as A; displaying more fluorescent zonations, less fluorescence, more euhedral crystal shapes and larger crystals (Schlattingen, 1144.62 m). (C) UV-fluorescence of TMD displaying fluorescent zonations and a stylolite cutting matrix dolomitization (Herdern, 1991.14 m). (D) UV-fluorescent zonations in TMD at the base of the Trigonodus Dolomit (Weiach, 854.24 m). (E) Mottled green–red CL texture of TMD at the top of the Pfaffnau borehole (1547.79 m; $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.70885$). (F) Corresponding UV-fluorescence image of E. Dark non-fluorescent crystals are anhydrite. (G) Mottled texture of TMD under CL from the middle of the Trigonodus Dolomite (Schlattingen, 1134.94 m; $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.7117$). (H) Corresponding UV-fluorescence image of G.

Under UV illumination, individual TMD crystals show up to three fluorescent zones: dull-yellow fluorescent cores surrounded by a thin bright-fluorescent overgrowth, in some crystals in turn overgrown by a non-fluorescent rim (Fig. 3.4D). Thicknesses of all these zones increase downwards in each borehole, paralleling the above-mentioned increase in crystal size. Fluorescence zonations do not strongly correlate with CL textures, which show mottled cores with multiple generations of dolomite, beginning with a dull-green generation and transitioning to more luminescent rims (Fig. 3.4E). The amount of mottling does not change between the top (Fig. 3.4E,F), middle (Fig. 3.4G,H) and bottom (Fig. 3.5A,B) of the unit. An exception to these trends are the deep wells (Berlingen, Herdern, Kreuzlingen and Lindau), which show homogeneous luminescence in TMD and abundant non-fluorescent, strongly luminescent cements occluding nearly all intercrystalline porosity (Fig. 3.5C,D). These cements are not observed in any of the other studied boreholes.

In some boreholes TMD and Hauptmuschelkalk Dolomites are associated with, and enclosed by, poikilotopic and replacive anhydrite cements, along with replacive anhydrite nodules or their late-dissolution vugs (Adams and Diamond, 2017). All anhydrite textures decrease in abundance with depth into the Hauptmuschelkalk.

4.1.2 Hauptmuschelkalk dolomite

Hauptmuschelkalk dolomite (HMD) consists of fine-grained to medium-grained (60 to 250 μm), sucrosic, planar-e, replacive rhombs disseminated in the Hauptmuschelkalk and in the base of the Trigonodus Dolomit (Adams and Diamond, 2017). The HMD generally cross-cuts facies boundaries but it can also form centimetre to decimetre thick beds in bioturbated mudstones. These beds are up to an order of magnitude more porous than the surrounding matrix. Hauptmuschelkalk dolomites are sometimes associated with glauconite-rich and pyrite-rich sediments and sub-mm dissolution vugs and stylolites. Dolomites in stylolite seams show none of the characteristics listed by Wanless (1979) as typical of an origin by pressure-solution (e.g., cloudy appearance, clay inclusions, overgrowing insoluble particles, containing smaller dolomite inclusions, or zonations in large rhombs).

The cores of HMD crystals show dull, speckled cathodoluminescence with up to two additional zones in some boreholes (Fig. 3.5E,F; Adams and Diamond, 2017). Under UV illumination, HMD crystals show dull fluorescence, although some rhombs are zoned similarly to TMD crystals at the base of the Trigonodus Dolomit (Fig. 3.5G). Fluorescence and cathodoluminescence characteristics of HMD do not change with depth.

Figure 3.5. Photomicrographs of TMD and HMD in sections stained with Alizarin Red S and potassium ferricyanide. (A) Euhedral TMD crystals from the base of the Trigonodus Dolomit, with similar mottled textures as in Fig. 3.4E and G (Bözberg, 94.66 m; $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.70876$). (B) UV-fluorescence image of euhedral TMD in same section as A. Yellow colour results from coating damage after CL imaging. (C) Deep-red zoned dolomite cements, differentiated from yellow TMD, found in all intercrystalline pores of the Lindau borehole (2246.67 m; $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.71106$). (D) Corresponding UV-fluorescence image of C. (E) CL image of HMD showing two stages of growth zonations, with rough edges (shown by arrows) indicating dissolution of the latest stage. The dark matrix is the Hauptmuschelkalk microspar. (F) Cross-polarized light image of E. Circular structures are LA-ICP-MS spot analyses. (G) Individual TMD in the Hauptmuschelkalk in a mass of non-fluorescent HMD a few metres below the base of the Trigonodus Dolomit. Compare with TMD zonations in Fig. 4D (Weiach, 859.05 m). (H) Dedolomite at the sharp boundary between the Trigonodus Dolomit and Hauptmuschelkalk (Schlattingen, 1145.54 m).

4.1.3 Dedolomite

Dedolomite is found stratigraphically at the transition from the Hauptmuschelkalk to the Trigonodus Dolomit and throughout the Hauptmuschelkalk. Dedolomitization affected all generations of TMD and HMD (Fig. 3.5H). Leaching appears to have commenced primarily on the outer rims of dolomite rhombs, prior to the subsequent generation of dolomite overgrowth. However, at the base of the Trigonodus Dolomit, leaching began within the cores of some dolomite rhombs.

4.2 Isotope and trace element geochemistry

4.2.1 Oxygen and carbon

Trigonodus matrix dolomites ($n = 92$) from nine boreholes show a narrow range of $\delta^{13}\text{C}_{\text{VPDB}}$ (-0.30 to 1.45‰) and a wide range of $\delta^{18}\text{O}_{\text{VPDB}}$ (-6.72 to -1.05‰) (Figs 3.6, 3.7 and 3.8; Tables 3.1 and 3.2). The $\delta^{13}\text{C}$ values increase slightly with depth within the top 10 m of the unit. Lower down, the $\delta^{13}\text{C}$ of *ca* 80% of all samples fall within a narrow range of 0.7 to 1.12‰ with an average of 0.93‰ . In contrast, $\delta^{18}\text{O}$ values clearly decrease with depth. No regional $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$ trends were identified. The one analysed dedolomite horizon, sampled at the contact with the underlying Hauptmuschelkalk, has $\delta^{18}\text{O}$ (-6.33‰) and $\delta^{13}\text{C}$ (1.06‰) values similar to those of dolomites elsewhere at the base of the Trigonodus Dolomit.

Figure 3.6. Values of $\delta^{13}\text{C}_{\text{VPDB}}$ versus $\delta^{18}\text{O}_{\text{VPDB}}$ in TMD, HMD and dedolomite. Circles: data from 9 boreholes (Table A3.2).

Hauptmuschelkalk dolomites ($n = 5$) show a limited range of $\delta^{18}\text{O}$ values from -6.63 to -5.97‰ (Table A3.2). In contrast to the TMD, no depth trend is observed. Carbon isotopes are slightly higher than TMD values and range from 0.98 to 1.99‰ .

Figure 3.7. Values of $\delta^{13}\text{C}_{\text{VPDB}}$ in matrix dolomites within the Trigonodus Dolomit (shaded) versus depth below the base of the Lettenkohle (i.e. top of Trigonodus Dolomit). Circles: data from 9 boreholes (Table A3.2).

4.2.2 Strontium isotopes

Strontium isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) analyses of TMD (Table 3.3) in the current study show a wide range of values (0.7080 to 0.7117), far higher than the marine $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70775 measured by Korte et al. (2003) on brachiopods of the Muschelkalk Sea. Hauptmuschelkalk dolomites show values around 0.710 , except for one horizon in the Trigonodus Dolomit (0.70876). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of TMD increases with depth within the Trigonodus Dolomit in all examined boreholes (Fig. 3.9). The strontium isotopic compositions of TMD do not correlate with any palaeogeographic trends but they appear to correlate weakly with oxygen isotopes (Fig. 3.10).

Strontium isotopes were also analysed in anhydrite nodules and in Hauptmuschelkalk limestones containing < 50 vol% dolomite. The limestones show $^{87}\text{Sr}/^{86}\text{Sr}$ ratios slightly higher than that of Middle Triassic sea water, in agreement with previous studies (Nagra, 2001; Ufrecht & Hölzl, 2006). Primary and diagenetic anhydrite nodules show similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to the dolomites surrounding them, including the increase in values with depth (Table 3.3; Fig. 3.9).

Table 3.3. Strontium and oxygen isotope analyses of primary anhydrite and matrix dolomite in the Trigonodus Dolomit and of dolomite in the Hauptmuschelkalk.

Borehole	Unit	Sample	Depth (m)	Depth from Lettenkohle (m)	Height above HMK ¹ (m)	Height above SS ² (m)	⁸⁷ Sr/ ⁸⁶ Sr (g/g)	Sr (μg/g)	δ ¹⁸ O‰ (VPDB)
Benken	Trigonodus Dolomit	Dolomite Matrix	840.10	28.75	8.37	46.23	0.70960		-4.55
Benken ³	Trigonodus Dolomit	Dolomite Matrix	828.14	16.79	20.33	58.19	0.70844	89	-3.78
Benken ³	Trigonodus Dolomit	Dolomite Matrix	836.46	25.11	12.01	49.87	0.70863	32	-4.39
Benken	Trigonodus Dolomit	Dolomite Matrix	816.16	4.81	32.31	70.17	0.70828		-2.76
Bözberg	Trigonodus Dolomit	Dolomite Matrix	72.88	14.46	23.20	72.51	0.70813		-3.31
Bözberg	Trigonodus Dolomit	Dolomite Matrix	64.82	6.40	31.26	80.57	0.70804		-3.20
Bözberg	Trigonodus Dolomit	Leached HMD	94.66	36.24	1.42	50.73	0.70876		-6.34
Lindau	Trigonodus Dolomit	Dolomite Matrix	2258.14	33.14	6.86	32.36	0.71122		-5.69
Lindau	Trigonodus Dolomit	Dolomite Matrix	2236.53	11.53	28.47	53.97	0.71056		-4.26
Lindau	Trigonodus Dolomit	Dolomite Matrix	2228.86	3.86	36.14	61.64	0.71005		-2.93
Lindau	Trigonodus Dolomit	Dolomite Matrix	2244.98	19.98	20.02	45.52	0.71060		-3.94
Pfaffnau	Trigonodus Dolomit	Dolomite Matrix	1548.30	4.64	26.70	59.57	0.70855		-3.38
Pfaffnau	Trigonodus Dolomit	Dolomite Matrix	1556.04	12.38	18.96	51.83	0.70926		-4.11
Schafisheim ⁴	Trigonodus Dolomit	Dolomite Matrix	1233.93	7.85	20.37	71.05	0.70812	85	-3.10
Schafisheim	Trigonodus Dolomit	Dolomite Matrix	1252.38	26.30	1.92	52.60	0.70967		-6.27
Schlattingen ⁶	Trigonodus Dolomit	Dolomite Oolite	1116.66	4.66	28.87	60.09	0.70886	45	-3.47
Schlattingen ⁶	Trigonodus Dolomit	Dolomite Matrix	1121.87	9.87	23.66	54.88	0.70869	44	-2.94
Schlattingen ⁶	Trigonodus Dolomit	Dolomite Matrix	1126.48	14.48	19.05	50.27	0.70979	35	-3.73
Schlattingen ⁶	Trigonodus Dolomit	Dolomite Matrix	1127.83	15.83	17.70	48.92	0.71016	36	-4.24
Schlattingen ⁶	Trigonodus Dolomit	Dolomite Matrix	1135.58	23.58	9.95	41.17	0.71170	35	-5.67
Siblingen ⁵	Trigonodus Dolomit	Dolomite Matrix	191.00	14.89	16.77	58.39	0.70979		-4.12
Weiach	Trigonodus Dolomit	Dolomite Matrix	846.73	28.17	10.32	50.93	0.70992		-4.42
Weiach	Trigonodus Dolomit	Dolomite Matrix	850.60	32.04	6.45	47.06	0.71045		-4.19
Weiach	Trigonodus Dolomit	Dolomite Matrix	820.67	2.11	36.38	76.99	0.70840		-3.64
Bözberg	Trigonodus Dolomit	Dolomite Matrix	94.66	36.24	1.42	50.73	0.70876		-5.21
Bözberg	Hauptmuschelkalk	Leached HMD	121.95	63.53	-25.87	23.44	0.71007		-6.63
Bözberg	Hauptmuschelkalk	Leached HMD	98.52	40.10	-2.44	46.87	0.70919		-6.54
Bözberg	Hauptmuschelkalk	Leached HMD	117.61	59.19	-21.53	27.78	0.71006		-5.95
Schafisheim	Trigonodus Dolomit	Primary Anhydrite	1234.67	8.59	19.63	70.31	0.70822		
Benken	Trigonodus Dolomit	Anhydrite Nodule	828.57	17.22	19.90	57.76	0.708763	1002	
Benken	Trigonodus Dolomit	Anhydrite Nodule	831.33	19.98	17.14	55.00	0.708802	1117	
Schlattingen ⁶	Trigonodus Dolomit	Anhydrite Nodule	1121.87	9.87	23.66	54.88	0.78461	1368	
Schlattingen ⁶	Trigonodus Dolomit	Anhydrite Nodule	1135.29	23.29	10.24	41.46	0.708997	1458	
Schlattingen ⁶	Hauptmuschelkalk	Limestone	1167.88	55.88	-22.35	8.87	0.708242	198	
Schlattingen ⁶	Hauptmuschelkalk	Limestone	1168.31	56.31	-22.98	8.44	0.708318	185	

¹Hauptmuschelkalk and ²Sulfatschichten. All ⁸⁷Sr/⁸⁶Sr measurements from this study except for: ³Nagra (2001), ⁴Pearson et al. (1991), ⁵Zeeh and Geng (2001) and ⁶Diamond et al. (2013)

Figure 3.8. Trends of $\delta^{18}\text{O}_{\text{VPDB}}$ in matrix dolomites within the Trigonodus Dolomit (shaded) versus their depth to the middle Muschelkalk Sulfatschichten in each examined borehole (Table A3.2). Above the grey field lies the Lettenkohle; below the grey field lies the Hauptmuschelkalk.

Figure 3.9. Values of $^{87}\text{Sr}/^{86}\text{Sr}$ in matrix dolomites and anhydrites within the Trigonodus Dolomit (shaded) versus depth to the middle Muschelkalk Sulfatschichten in each examined borehole (Table 3.3).

Figure 3.10. Correlations between $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}_{\text{VPDB}}$ in matrix dolomites in the TMD and in the underlying HMD (Table 3.3).

4.3 Trace element geochemistry

The TMD and HMD have similar Mg, Sr, Fe and Mn concentrations, while the calcitic microspar shows higher Sr and lower Fe and Mn concentrations with respect to the TMD and HMD (Table 3.4). Laser ablation ICP-MS of calcitic microspar in one thin section shows that it is a low-magnesium calcite with on average 145 $\mu\text{g/g}$ Sr, 113 $\mu\text{g/g}$ Fe, and 45 $\mu\text{g/g}$ Mn (Table 3.4). Trigonodus matrix dolomites are nearly stoichiometric (48.8 ± 1.0 mole% Mg), have variable Fe contents (680 ± 485 $\mu\text{g/g}$), are Mn-enriched (78 ± 3 $\mu\text{g/g}$), and are low in Sr (36 ± 28 $\mu\text{g/g}$). No regional or depth trends in dolomite stoichiometry were observed. Hauptmuschelkalk dolomites also approach stoichiometric values (47.7 ± 1.1 mole% Mg), are Fe-rich (1194 ± 641 $\mu\text{g/g}$), Mn enriched (97 ± 10 $\mu\text{g/g}$) and have Sr contents slightly higher than TMD (68 ± 16 $\mu\text{g/g}$). Strontium concentrations in TMD decrease with depth (Table 3.3). Trigonodus matrix dolomites and HMD have Rb/Sr ratios of around 1:50. Therefore, using an initial age of 242 Ma and an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70775 for Upper Muschelkalk sea water (Korte et al., 2003), rubidium decay is calculated to have insignificantly increased the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio to 0.70782.

Table 3.4: Petrographic and geochemical comparison between Trigonodus Matrix Dolomites (TMD) and Hauptmuschelkalk Dolomites (HMD) and microspar presented as mean $\pm$ 1 σ .

Sample Type	Stratigraphic Distribution	CL	UV-fluorescence	Mg (mole %) ¹	Sr ($\mu\text{g/g}$) ²	Fe ($\mu\text{g/g}$) ²	Mn ($\mu\text{g/g}$) ²	Rb/Sr (g/g) ²	$\delta^{13}\text{C}$ (‰ VPDB)	$\delta^{18}\text{O}$ (‰ VPDB)	$^{87}\text{Sr}/^{86}\text{Sr}$ (g/g)
TMD	Trigonodus Dolomit	Mottled, faint zonations	Bright cores, dull zonations	48.8 $\pm$ 1.0 (n = 79) 45.7–50.5	36 $\pm$ 28 (n = 22) 18–150	680 $\pm$ 485 (n = 22) 201–1779	78 $\pm$ 3 (n = 22) 73–84	1:58	0.79 $\pm$ 0.30 (n = 92) –0.30 to 1.33	–3.91 $\pm$ 1.10 (n = 92) –6.72 to –1.05	0.709403 $\pm$ 0.00102 (n = 24) 0.70804 to 0.7117
HMD	Hauptmuschelkalk and lower Trigonodus Dolomit	Mottled, non-luminescent zonations	Dull, no zonations	47.7 $\pm$ 1.1 (n = 41) 45.3–49.5	68 $\pm$ 16 (n = 29) 44–124	1194 $\pm$ 641 (n = 29) 495–3236	97 $\pm$ 10 (n = 29) 84–119	1:46	1.46 $\pm$ 0.42 (n = 5) 0.98 to 1.99	–6.42 $\pm$ 0.28 (n = 5) –6.64 to –5.97	0.70952 $\pm$ 0.00065 (n = 4) 0.70876 to 0.71007
Microspar ³	Hauptmuschelkalk	Mottled	Weak	0.9 $\pm$ 0.6 (n=12) 0.5–2.8	149 $\pm$ 56 (n=12) 87–237	113 $\pm$ 39 (n=12) 23–161	45 $\pm$ 8 (n=12) 34–64	1:149	0.41 $\pm$ 0.08 (n = 5) 0.30 to 0.51	–5.39 $\pm$ 0.55 (n = 5) –6.03 to –4.60	0.7083 (n = 2) 0.7082 & 0.7083

¹Analyses by microprobe on dolomites from multiple boreholes. Microspar measurements by LA-ICP-MS.

²Analyses by LA-ICP-MS on Bözberg, 89.32 m for the TMD and Bözberg, 121.95 m for the HMD and microspar.

³Microspar stable isotope ratios from Adams and Diamond (2017).

4.4 Fluid inclusions

Temperatures of final melting of ice in rare, *ca* 3 μm diameter fluid inclusions in TMD vary between -25 and -10 $^{\circ}\text{C}$ with an average of -21 $^{\circ}\text{C}$ ($n = 6$). The temperatures below -21 $^{\circ}\text{C}$ (H_2O – NaCl eutectic) reveal the presence of salts such as CaCl_2 and MgCl_2 in addition to NaCl . The average salinity of these fluids in terms of the H_2O – NaCl model system is 22 wt.% NaCl , based on the calibration of Bodnar (1993) for solutions saturated in H_2O -vapour. The lack of vapour in the inclusions implies a slightly higher salinity for a given ice-melting temperature, thus the inclusions on average contain > 22 wt.% NaCl equivalent.

4.5 Isochore maps

Isochore maps in this study reveal that the thicknesses of the Upper Muschelkalk and its subunits, and the fraction of dolomite in the Upper Muschelkalk, are related to Anisian–Ladinian palaeoshoreline positions (Fig. 3.11). The Upper Muschelkalk is thickest in the basin centre and in north-central Switzerland, and thinnest near the palaeoshorelines of the Middle Triassic palaeohighs (Fig. 3.11A). The Hauptmuschelkalk also thins towards the palaeoshorelines; however, the unit is thicker on the western palaeoshoreline than the eastern shoreline (Fig. 3.11B). In contrast, the *Trigonodus* Dolomit thickens from the basin centre towards both palaeoshorelines (Fig. 3.11C). The dolomitized fraction of the Upper Muschelkalk varies from 100 vol% along the palaeoshoreline of the Brabant Massif, to < 10 vol% along a NNE-SSW channel on the border of western Switzerland, to > 50 vol% off the palaeoshoreline of the southern Vindelician High (Fig. 3.11D). Dolomite fractions decrease northwards into Germany in agreement with the isopach maps of Alesi (1984).

5 Discussion

Several studies have attributed the low $\delta^{18}\text{O}$, high $^{87}\text{Sr}/^{86}\text{Sr}$, stoichiometric elemental compositions, depleted strontium-concentrations and high iron-concentrations of TMD to recrystallization (Schauer & Aigner, 1997; Zeeh & Geng, 2001; Tucker & Marshall, 2004). Each of these studies contends that earlier dolomites formed during evaporation or seepage-reflux and then recrystallized during shallow burial. Dolomite recrystallization may have occurred progressively following burial in ambient marine pore fluids, or by the introduction of meteoric fluids (Zeeh & Geng, 2001). Progressive recrystallization of dolomites is known to occur ubiquitously during shallow burial (Land et al., 1975; Machel & Mountjoy, 1986; Hardie, 1987; Land, 1991; Kupecz et al., 1993) and results in dolomites with depleted Sr-concentrations, increasing stoichiometry, increasing ordering, mottled CL, low oxygen-isotopic ratios, radiogenic strontium-isotopic ratios, bimodal crystal sizes and increased crystal sizes (McKenzie, 1981; Bein & Land, 1983; Kupecz et al., 1993; Kupecz & Land 1994; Reinhold, 1997; Machel, 2004). Although TMD display all these characteristics, they also show

vertical geochemical and isotopic trends, which indicate fluid movement during dolomite crystallization (Machel, 1988). Therefore, these trends cannot be explained by the progressive recrystallization of dolomite in ambient pore fluids and the trends must instead reflect the migration of dolomitizing or later recrystallizing fluids.

However, the following section demonstrates that late recrystallization by a single recrystallizing fluid also cannot explain the observed petrographic and isotopic trends of the Trigonodus Dolomit. These trends can only be explained by the mixing of two distinct fluids during dolomitization. Focus is placed on constraining the pathways, timings and origins of these fluids, and on incorporating them into a wider stratigraphic framework.

5.1 Dolomite distribution and petrography

The most important guides in determining the origin of dolomite are its body geometry, geochemistry and lithological associations (Warren, 2000). The Trigonodus Dolomit is contiguous with the base of the Lettenkohle across the entire southern CEB. In the Swiss Molasse Basin it shows no systematic changes in thickness down its regional, SE-directed 4° dip towards the Alps and no thickness changes occur near fault structures (Sommaruga et al., 2012). Therefore, the current thickness of the Trigonodus Dolomit is interpreted to reflect its Triassic thickness immediately following any erosion prior to deposition of the Lettenkohle.

This basin-wide geometry of the Trigonodus Dolomit can only be explained by dolomitizing fluid(s) that migrated through the Upper Muschelkalk carbonate ramp on a regional scale. Ascent of a fluid from depth is ruled out by several features; the abundance of calcite in the Hauptmuschelkalk, the lack of hydrothermal-dolomite textures and the lack of any vertical or plume-like dolomite bodies that are common to fault-associated dolomites (Warren, 2000). Migration could therefore have been lateral over great distances, vertically downwards, or some combination of the two. The primary fluid inclusions in the TMD indicate that the dolomitizing fluids were extremely dense, containing > 220 g/kg NaCl equivalent. Therefore, density-driven migration of the fluid over long lateral distances may have been feasible.

The fact that the thickest sections of Trigonodus Dolomit and the most completely dolomitized fractions of the Upper Muschelkalk occur near palaeoshorelines (Fig. 3.11) suggests that the dolomitizing fluids themselves originated along palaeoshorelines. Consistent with this idea, the thinning of the dolomite towards the basin centre indicates that brines were produced and migrated laterally into the basin from the southwestern and southeastern palaeoshorelines (Fig. 3.11D). Dolomitization along palaeoshorelines cannot be explained by influx of Mg-rich fluids from compacted and dewatered claystones on nearby palaeohighs (i.e. via burial dolomitization), because the palaeohighs were not buried until the Late Jurassic (Ziegler, 1990) when the Upper Muschelkalk was already at > 700 m in depth (Mazurek et al., 2006). Since dolomitization occurred prior to any

significant burial and stylolitization, its clear palaeogeographic control must reflect other environments that created dolomitizing fluids. These environments have been characterized as restricted hypersaline lagoons or sabkhas based on palaeogeographic reconstructions, facies characteristics and the increasing number of anhydrite cements, anhydrite nodules and anhydrite dissolution vugs towards the top of the Upper Muschelkalk (Schauer & Aigner, 1997; Koehrer et al., 2010; Franz et al., 2015). Hypersaline environments were isolated from the open marine Upper Muschelkalk Sea by a belt of shoaling bodies rimming the Vindelician High at a distance of > 50 km basinward (Merki, 1961; Aigner, 1985). A hypersaline environment 50 km wide and stretching from southern Germany into central Switzerland would have produced refluxing brines over an area > 8000 km² along the margin of the Vindelician High. While seepage-reflux can be limited to the extent of the surface water-bodies, as in island dolomites (Budd, 1997), it is not necessarily so (Jones & Xiao, 2005) and large-scale seepage-reflux can transport brines far into the centres of basins (Jones et al., 2002).

Figure 3.11. Isochore maps of the Upper Muschelkalk in the Southern CEB produced by kriging borehole data (Table A3.1). (A) Approximate thickness (m) of the Upper Muschelkalk. (B) Approximate thickness (m) of the Hauptmuschelkalk. (C) Approximate thickness (m) of the Trigonodus Dolomit. (D) Approximate dolomitized fraction of the Upper Muschelkalk (vol%).

Petrographic textures also support the migration of dolomitizing fluid(s). Dolomite crystal size increases and changes from anhedral to euhedral crystals with depth, which is characteristic of seepage-reflux dolomites and migrating recrystallizing fluids (Kupecz et al., 1993; Wahlman, 2010) and can be explained by decrease in the dolomite saturation state of the fluids (Sibley & Gregg, 1987). Sharp CL and UV-fluorescence zonations indicate multiple dolomite generations and repeated crystallization in reducing fluids with different geochemistries and organic compounds. The overprinting mottled CL texture suggests the dolomites were recrystallized (Kupecz et al., 1993) or formed in mixed fluids (Gaswirth et al., 2007). In contrast, the distinct fluorescent–non-fluorescent zonations suggest that dolomites were indeed not recrystallized. Dolomite fluorescence reflects the amount of aqueous humic compounds (Dravis & Yurewicz, 1985; Ramseyer et al., 1997), implying that large non-fluorescent zones in TMD at base of the Trigonodus Dolomit crystallized in fluids lacking such substances, while dolomites at the top of the unit formed predominantly in organic-rich fluids. The likeliest source of organic-rich fluids was sea water, whereas non-fluorescent zonations have been attributed to freshwater diagenesis (Dravis & Yurewicz, 1985).

In summary, based on the distribution of the dolomite body, its associated sulphate textures, its fluid inclusions, mineralogy and petrography, initial dolomitization is interpreted to have begun shortly after burial due to reflux of hypersaline brine. The new geochemical and isotopic data in this study, however, point to a more complex dolomitization history than simple migration of an evaporative brine through a sea water saturated carbonate precursor.

5.2 Strontium isotope compositions

As strontium isotopes do not fractionate during diagenesis (Faure & Powell, 1972), the isotopic ratio recorded in a carbonate represents that of its parent or recrystallizing fluid. The marine $^{87}\text{Sr}/^{86}\text{Sr}$ curve for the Triassic has been established by Korte et al. (2003) and shows a range from 0.7073 to 0.7082 and a value of 0.70765 for the Tethys during the Anisian/Ladinian. The strontium isotopic ratio of the Upper Muschelkalk Sea, however, is slightly elevated to 0.70775, which Korte et al. (2003) ascribe to the influx of fresh runoff water from the exposed radiogenic basement highs ($^{87}\text{Sr}/^{86}\text{Sr} \leq 0.718$).

Pre-dolomitization mixing of sea water with runoff-derived groundwater from the Vindelician High has been shown to have neomorphosed aragonite micrite to low-magnesium calcite microspar in the Hauptmuschelkalk (Adams & Diamond, 2017). This mixing could also explain the slightly elevated microspar $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Initial aragonitic micrites would have had strontium concentrations in the thousands of $\mu\text{g/g}$ (Tucker & Wright, 1990), and their $^{87}\text{Sr}/^{86}\text{Sr}$ ratio would have reflected Middle Triassic sea water. In contrast, the strontium concentrations in microspar are only *ca* 150 to 190 $\mu\text{g/g}$. During neomorphism, abundant marine-derived Sr would have been released from the recrystallizing aragonite into the mixed pore waters, which initially contained low Sr concentrations but high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from rock-water interactions with the gneissic Vindelician High (Korte et al.,

2003). This mass balance effect (e.g. Gieskes et al., 1986) may explain the microspar $^{87}\text{Sr}/^{86}\text{Sr}$ value of ~ 0.7083 (Table 3.3), only slightly above that of the sea water. After neomorphism, the calcite would have been in chemical equilibrium with the groundwater and so no further calcite recrystallization could have occurred. Thus, the calcite likely records the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the water–rock mixture at the time of its initial crystallization prior to matrix dolomitization (Adams & Diamond, 2017).

The anhydrite nodules and TMD have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios significantly more radiogenic than any Middle Triassic sea waters. Moreover, their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios display a striking trend beginning with values near Upper Muschelkalk sea water at the top of the unit and showing progressively more radiogenic values downwards (Fig. 3.9). Since this depth trend is observed throughout the $>2000\text{ km}^2$ extent of the Upper Muschelkalk in Switzerland, it must have been caused by a regional hydrological event.

Prior to using the $^{87}\text{Sr}/^{86}\text{Sr}$ depth trend to constrain the source of the dolomitizing fluid, it must be demonstrated that this trend is an original feature of the Trigonodus Dolomit, not the result of a later overprint (e.g., related to the Cenozoic Alpine orogeny). Today the northern margin of the Trigonodus Dolomit within Switzerland is an aquifer, in which infiltrating low-salinity waters ($<10\text{ g/kg NaCl-eq.}$) have dissolved anhydrite nodules and mixed with the original dolomitizing hypersaline brine (Aschwanden et al., 2017). The low-salinity fluid has extremely high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios up to 0.717, as recorded by secondary calcite in cross-cutting fractures, and so potentially it could have imposed the observed depth trends during the Neogene via recrystallization. However, the same depth trend is observed in low-permeability zones of the Trigonodus Dolomit where anhydrite nodules are still preserved, i.e. where no appreciable volumes of Neogene low-salinity fluid have infiltrated the formation. Moreover, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios > 0.710 occur in TMD in SW Germany (Zeeh & Geng, 2001), well outside the influence of the Alpine orogeny. Therefore, the depth trends shown in Fig. 3.9 must indeed have an early diagenetic origin.

Whereas the $^{87}\text{Sr}/^{86}\text{Sr}$ values at the top of the depth trend could be explained by reflux of evaporated sea water brine, the lower segment of the trend requires progressive addition of radiogenic ^{87}Sr , either during the initial dolomitization event or during a possible subsequent recrystallization event. For the case of initial dolomitization, only one source of ^{87}Sr -enriched fluid is conceivable; freshwater runoff from the crystalline basement exposed in the Vindelician–Bohemian High ($^{87}\text{Sr}/^{86}\text{Sr} \leq 0.718$). This is the same freshwater that deposited the terrestrial claystones in the Lettenkohle ($^{87}\text{Sr}/^{86}\text{Sr} \leq 0.712$; Fig. 3.12), which overlie the Trigonodus Dolomit.

For the alternative case of recrystallization, both the crystalline basement at 100 to 500 m depth below the Trigonodus Dolomit (with $^{87}\text{Sr}/^{86}\text{Sr}$ identical to that in the Vindelician–Bohemian High; Fig. 3.12) and the infiltration of basement runoff water, either laterally or from above the Trigonodus Dolomit are, at first sight, potential sources for radiogenic Sr. However, the underlying crystalline basement can be ruled out because of the presence of thick impermeable strata below the Trigonodus

Dolomit (i.e. the Middle Muschelkalk sulphates, halites and tens of metres of clays), which would have acted as an effective and spatially extensive hydraulic barrier to vertical flow. Infiltration of runoff water from above the Trigonodus Dolomit can also be excluded because, although the Vindelician High could have provided $^{87}\text{Sr}/^{86}\text{Sr}$ -enriched waters over an extensive area during the early Ladinian regression, their downward infiltration into the Trigonodus Dolomit would have produced decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ values with depth, which is the opposite of the observed trends (Fig. 3.9). Recrystallization by lateral infiltration of groundwaters from the Vindelician High would also fail to produce the $^{87}\text{Sr}/^{86}\text{Sr}$ depth trends and would instead have produced a horizontal trend in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Müller et al., 1990). Post-dolomitization recrystallization by a single fluid is therefore an untenable mechanism to explain the $^{87}\text{Sr}/^{86}\text{Sr}$ depth trend of the dolomite.

Figure 3.12. Schematic summary of $^{87}\text{Sr}/^{86}\text{Sr}$ values in the Trigonodus Dolomit and in surrounding units. Dots: individual samples. Rectangles: range of data from the studies a–g listed below. Representative data are taken from various boreholes to illustrate main trends. Average thicknesses are based on NAGRA boreholes within Switzerland (Table A3.1). Individual measurements in the Trigonodus Dolomit are from this study (Table 2). a) Pearson et al. (1991); b) Nagra (2001); c) Zeeh & Geng (2001); d) Korte et al. (2003); e) Ufrecht & Hölzl (2006); f) De Haller et al. (2014); g) this study.

Alternatively, mixing of two distinct fluids during dolomitization could conceivably have produced dolomites with a range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Adams & Diamond (2017) showed that Vindelician groundwaters were flowing through the Upper Muschelkalk immediately prior to matrix

dolomitization. Had dolomite formed from reflux of brines into $^{87}\text{Sr}/^{86}\text{Sr}$ -enriched groundwater, then mixed strontium signatures from the two waters would have been imparted to the product dolomites.

To test the feasibility of this reflux hypothesis for the Trigonodus Dolomit, the effect of mixing hypersaline brines and groundwaters was simulated using the equations of Banner & Hanson (1990) and end-member fluid compositions from the Abu Dhabi sabkha (Butler, 1969; Wood et al., 2002) (Fig. 3.13A). The mixing curve shows that increasing admixture of groundwater results in a trend that follows the data points in Fig. 3.13A, reproducing the observed vertical depth trends in strontium concentrations (Fig. 3.13B) and isotopic compositions (Fig. 3.13C,D) of the dolomite.

While recrystallization can account for slightly elevated matrix calcite $^{87}\text{Sr}/^{86}\text{Sr}$ values, dolomite recrystallization by any one migrating fluid is incapable of producing the observed downwards increase in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Only mixing of hypersaline brines with infiltrating groundwaters is consistent with the observed Sr isotope depth-trend.

Figure 3.13. Correlations between key geochemical indicators in the Upper Muschelkalk. All data from this study. (A) Dolomite Sr concentrations versus $^{87}\text{Sr}/^{86}\text{Sr}$ values in the Trigonodus matrix dolomite (TMD). Curve shows mixing ratios of a hypersaline brine similar to that in the modern Abu Dhabi sabkha (Butler, 1969) with 18000 µg/g Mg, 4000 µg/g Ca, 30 µg/g Sr, 300 g/kg salinity and a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio near Upper Muschelkalk sea water (0.708), mixed with a groundwater similar to that of Abu Dhabi sabkha groundwaters (Wood et al., 2002) with 2000 µg/g Mg, 2000 µg/g Ca, 2.5 µg/g Sr, 100 g/kg salinity and a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of Vindelician High runoff (ca 0.712; Korte et al., 2003). Strontium concentrations in dolomite calculated using $K_D^{\text{Sr-Ca}} = 0.06$ (Baker and Burns, 1985). Labelled in blue is the percentage of brine within the mixture and in parenthesis the salinity in g/kg; and in red the fluid Mg/Ca weight ratios, calculated according to Banner & Hanson (1990). (B) Dolomite Sr concentrations from multiple boreholes versus their height above the Sulfatschichten (SS). (C) Oxygen isotopic ratios of all analysed TMD samples versus their height above the SS. A regional downwards decrease in the ratios is clearly observed. (D) Strontium isotope analyses of all HMD and TMD samples, with the Lindau borehole highlighted, versus their height above the SS. The downward increase in $^{87}\text{Sr}/^{86}\text{Sr}$ values of TMD and Lindau samples is emphasized by a sketched arrow.

5.3 Stable C–O isotope compositions

Carbon concentrations in limestones are often 2 to 4 orders of magnitude greater than those in diagenetic fluids (Banner & Hanson, 1990), therefore the $\delta^{13}\text{C}$ of replacive dolomites is often buffered by their precursor limestones. In line with this behaviour, the $\delta^{13}\text{C}$ values of the TMD (Fig. 3.7) are indeed comparable to those of the Hauptmuschelkalk limestones (Schauer & Aigner, 1997; Adams & Diamond, 2017), indicating that the TMD inherited its $\delta^{13}\text{C}$ from its precursor limestones. Carbon isotope values of early groundwater cements are also buffered by the carbonate matrix and indicate that these groundwaters contained little dissolved organic matter (Adams & Diamond, 2017). Thus, the upwards decrease in $\delta^{13}\text{C}$ visible in Fig. 3.7 is interpreted to reflect increasing input of organic carbon from terrestrial sources during initial limestone sedimentation (Allan & Matthews 1977, 1982). This upwards decrease is a widespread feature of the Upper Muschelkalk (Zeeh & Geng, 2001).

The oxygen isotope ratios of the TMD (Fig. 3.8) are significantly depleted relative to values expected for Middle Triassic marine dolomites (Schauer & Aigner, 1997). Moreover, when plotted relative to their height above the Middle Muschelkalk sulphates, the TMD isotope values show a regional downwards-depletion trend (Figs 3.8 and 3.13C). Since oxygen isotopes fractionate as a function of temperature, this trend could in principle reflect a temperature gradient during dolomitization. However, a strong gradient is ruled out by the shallow depth of formation and modest thickness of the Trigonodus Dolomit. The trend is therefore attributed to the mixing of the isotopically distinct hypersaline brine and infiltrating groundwater alluded to above. Prior to dolomitization, meteoric groundwater temperatures averaged around 32 °C (Adams & Diamond, 2017), whereas the hypersaline brines were likely warmer, as implied by their association with anhydrite (Jones & Xiao, 2005). Using the dolomite–water fractionation equation of Vasconcelos et al. (2005), which was derived from hypersaline, low temperature dolomites like the TMD, and a precipitation temperature of 40 °C, the TMD are calculated to have formed from waters with $\delta^{18}\text{O}_{\text{SMOW}}$ *ca* –4‰ at the base of the Trigonodus Dolomit and from waters with *ca* 2 ‰ at the top. The latter values are somewhat lower than those of modern hypersaline brines, which can reach $\delta^{18}\text{O}_{\text{SMOW}} > 5\text{‰}$ (McKenzie et al., 1980). This suggests that the dolomites that were originally at the top of the Trigonodus Dolomit and that were eroded away by prograding continental environments may have been isotopically heavier. Based on this inference, the top of the depth trend in Fig. 3.13C does not begin at the end-member brine composition, but at a certain distance along the mixing line towards the groundwater end-member. Similarly, the oxygen isotope values of the dolomitizing fluids at the base of the Trigonodus Dolomit are slightly more positive than those of the end-member meteoric groundwater ($\delta^{18}\text{O}_{\text{SMOW}} = -4.4\text{‰}$; Adams & Diamond, 2017), which suggests that at least a small fraction of the refluxing ^{18}O -enriched brine reached the base of the unit.

5.4 Dolomitization model

The geochemical, isotopic and petrographic evidence presented above is consistent with dolomitization of the Trigonodus Dolomit having resulted from reflux of hypersaline brine downwards into a pre-existing, regionally extensive aquifer saturated in meteoric-derived groundwater. The proposed dolomitization model is similar to mixing-zone dolomitization models that invoke mixing of hypersaline brine with low-salinity water (Muir et al., 1980; Gill et al., 1995; Meyers et al., 1997). Such models have been criticized owing to their resulting low salinities, low aqueous Mg/Ca ratios and small-volume mixing-zones (Hardie, 1987; Machel, 2004). However, the model in this study differs from others in three respects. First, it invokes flow of saline rather than fresh groundwaters, such that salinity remains high enough to dolomitize throughout the mixing spectrum (Fig. 3.13A). Second, the mixed fluids (Fig. 3.13A) retain Mg/Ca > 1 owing to the high Mg/Ca ratio of the evaporative-brine end-member and the Mg-enriched nature of the groundwater end-member, such that dolomitization of limestone is feasible across all mixing fractions (Meyers et al., 1997). Third, this model envisages seepage-reflux from a hypersaline back shoal environment as an effective solute transport mechanism, rather than dolomitization in a mixing-zone. As discussed above, this would provide an enormous environment capable of producing dolomitizing brines across the southern CEB.

The involvement of these two contrasting fluids requires that an arid environment caused significant evaporation of the Upper Muschelkalk Sea while simultaneously providing sufficient groundwater recharge into the basin. These conditions were met at the conclusion of the deposition of the Upper Muschelkalk (Fig. 3.14A), when the southwards-prograding continental Lettenkohle environments reached the southern CEB (Franz et al., 2015). Thus, meteoric runoff from the Lettenkohle and Vindelician High supplied up to 25 vol % of the water in the Upper Muschelkalk Sea (Korte et al., 2003, 2005). Prior to dolomitization some of these meteoric groundwaters, which presumably had been long stored in fracture networks within the Vindelician High, percolated seaward through tens of kilometres of Upper Muschelkalk sediments, driven by the hydraulic gradient induced during an early Ladinian lowstand (Adams and Diamond, 2017; Fig. 3.14B). Direct evidence for these groundwaters includes Upper Muschelkalk meteoric cements (Adams & Diamond, 2017) and elevated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in primary anhydrites of the Trigonodus Dolomit. Following this percolation the pore water in the entire *ca* 80 m thick sediment layer above the impermeable Sulfatschichten had a $\delta^{18}\text{O}_{\text{VSMOW}}$ value of around -4.4‰ and a $^{87}\text{Sr}/^{86}\text{Sr}$ value of at least 0.712 (Fig. 3.14C).

Figure 3.14. Dolomitization model of the Trigonodus Dolomit and potential fluid flow interactions at the end of the Upper Muschelkalk deposition. Vertical cross-sections are also shown for pore water (solid line) and carbonate (dashed line) values of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ (VPDB for carbonates; VSMOW for pore water). For simplicity the Dolomit der Anhydritgruppe is not shown in this model. (A) Initial Upper Muschelkalk Sea with aragonite matrix and seawater $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$. (B) The Upper Muschelkalk Sea recedes and coastal sabkhas are developed. Vindelician groundwater begins to flow into the basin on top of the middle Muschelkalk evaporites, and becomes denser through the dissolution of near-shore evaporites (note the asterisk).

Although the groundwaters in this model began as low-density freshwaters, they certainly increased in salinity and hence density during their lateral flow through the carbonate ramp due to groundwater evaporation, mixing or dissolution of evaporite minerals (Baltzer et al., 1994; Wood et al., 2005). In the Upper Muschelkalk ramp, significant evaporation and mixing evidently did not occur, because the groundwater retained low $\delta^{18}\text{O}$ values far into the basin. Instead, continental freshwaters likely dissolved pre-existing evaporites near the Vindelician shoreline (Geyer and Gwinner, 2011; asterisk in Fig. 3.14B), thereby increasing their density without appreciably changing their $\delta^{18}\text{O}$ value (Clark, 2015). During the early Ladinian sea-level rise, the large density contrast would have caused the encroaching sea water to float on the denser groundwater rather than displace it (Fig. 3.14C). Meanwhile, the dense groundwater would have continued to flow towards the basin without mixing significantly with the overlying sea water (Yeichieli and Wood, 2002).

Figure 3.14 (continued). Dolomitization model of the Trigonodus Dolomit (continued) (C) Extensive lateral percolation of Vindelician groundwater through the Upper Muschelkalk displaces connate seawater and recrystallizes aragonite to calcite. The calcite records the slightly elevated $^{87}\text{Sr}/^{86}\text{Sr}$ value at the time of its crystallization. Sea-level rises and sea water floods the lagoon but effectively floats upon the now denser groundwaters. Trapped sea water in the back shoal lagoon begins to evaporate. (D) Advanced evaporation in the lagoon causes lobate plumes of hypersaline brines to begin refluxing downwards into the groundwater-saturated sediments, initiating dolomitization.

The increase of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in diagenetic anhydrite nodules with depth in the Trigonodus Dolomit (Fig. 3.12) and dolomite inclusions within the nodules indicate that these nodules precipitated during dolomitization, as is common during seepage-reflux dolomitization (Machel, 2004). However, these nodules only precipitated following the formation of primary anhydrite (Adams and Diamond, 2017). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of primary anhydrite in the Trigonodus Dolomit are higher than that of Middle Triassic sea water, indicating the early influx of radiogenic strontium into the developing coastal sabkha. Sediments preserved by early chertification of primary anhydrites lack dolomites, demonstrating that dolomitization occurred after establishment of the coastal sabkha at the top few metres of the Trigonodus Dolomit (Adams and Diamond, 2017). This implies a sea-level rise and development of a new environment that was capable of producing dolomitizing brines following

groundwater infiltration (Fig. 3.14C). Although the nature of this environment is unknown due to erosion upon deposition of the Lettenkohle (Franz et al., 2013), evidence elsewhere shows that restricted lagoons and hypersaline conditions existed across the southern CEB at this time (Fig. 3.3; Schauer and Aigner, 1997; Franz et al., 2015).

Figure 3.14 (Continued). (E) Significant advective groundwater flow mixes with and merges the refluxing brine plumes, resulting in laterally uniform, vertical isotopic gradients. Dolomite proceeds to replace calcitic limestone and acquires the geochemical and isotopic characteristics of the mixed waters. The uppermost dolomites, with the most positive $\delta^{18}\text{O}$ values, are likely eroded by the prograding continental environment.

5.5 Mechanism of brine reflux

Upon reflux, the brines displaced the sea water and groundwater within the Upper Muschelkalk as they migrated downwards and laterally into the basin (Fig. 3.14D). For such reflux to account for the isotopic trends and petrographic textures documented above, two scenarios are proposed: (i) brine reflux into stationary groundwater; or (ii) brine reflux into horizontally advecting groundwater. Both processes would produce geochemically, isotopically and texturally similar dolomites. However, the brine-plume geometries and the resulting dolomite bodies would differ between the two scenarios.

Regarding the first scenario, brine reflux into stationary groundwaters in experimental and natural systems begins as swarms of vertical, lobate fingers that progressively coalesce and disperse as they penetrate deeper (Wooding et al., 1997; Simmons et al., 1999; Van Dam et al., 2014). Multiple generations of dolomite may be produced in this scenario, reflecting the unstable plume geometry and lateral migration of the brine source. As reflux continues, groundwater is displaced upwards between the brine fingers in small convection cells (Fig. 3.14D). In the Trigonodus Dolomit such upwelling groundwaters could conceivably have recrystallized some of the newly formed dolomites, and if the dolomites at the base interacted with more pore volumes of groundwaters than those at the top of the formation, the observed trends in $\delta^{18}\text{O}$ and radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ could perhaps have been produced.

However, several observations contradict this scenario. Foremost, the dolomites at the base of the Trigonodus Dolomit are not more recrystallized than those at the top of the formation (Fig. 3.4). Additionally, the TMD is equally stoichiometric throughout the unit. Further, it is difficult to imagine how the observed basin-wide, monotonic $^{87}\text{Sr}/^{86}\text{Sr}$ depth trend could be established by relatively chaotic convection cells. Finally, this scenario is unlikely to produce the relatively uniform thickness of the Trigonodus Dolomit in Switzerland and its lack of deep lobate bodies of dolomite.

A relatively uniform thickness of dolomite requires some spatially extensive hydraulic control to limit the depth to which dolomitizing fluids penetrate. No low-permeability confining unit exists at the Trigonodus Dolomit–Hauptmuschelkalk transition. However, the second of the above scenarios provides a suitable hydraulic control. Laboratory experiments and computer modelling demonstrate that horizontal aquifer flow controls the geometry and distribution of refluxing lobate brine-plumes (Oostrom et al., 1992; Wooding et al., 1997; Pal et al., 2014). Pal et al. (2014) demonstrated that fingering was entirely suppressed and a horizontally uniform, vertical mixing-gradient of solutes was established when horizontal advection exceeded a threshold value (Fig. 3.14E). Such mixing gradients show vertical isotopic trends similar to those recorded in the Trigonodus Dolomit (Jacobson et al., 1991). Thus, in accordance with observations in this study, dolomites produced at the base of the column would show isotopic properties reflecting basal groundwaters, while dolomites at the top would reflect refluxing fluids. Following brine reflux, some dolomites could have recrystallized as the aquifer returned to a groundwater-dominated system.

In both scenarios, groundwaters in the Hauptmuschelkalk would have been generally undersaturated with respect to dolomite. To explain the occurrences of localized stratiform layers of HMD there needs to have been increased fluxes of Mg-bearing fluids or additional Mg sources in the limestone beds. Permeable beds, such as the observed bioturbated mudstones, could have facilitated influx of Mg-rich brines to enhance TMD-type dolomite nucleation in localized layers. Also, the common association of these dolomite layers with certain Mg-enriched features (e.g., specific bioclasts and glauconite-rich horizons) suggests that they acted as nucleation sites for dolomitization, as is the case in lab-grown dolomites (Sibley et al., 1994). Textures under UV light demonstrate that these sparse TMD eventually recrystallized into HMD (Fig. 3.5G). The non-fluorescence of HMD shows that recrystallization occurred in organic-poor fluids, like the early groundwaters (Adams and Diamond, 2017). Using the dolomite–water fractionation factor of Vasconcelos et al. (2005) and a temperature of 40 °C, HMD is calculated to have recrystallized from fluids with an average $\delta^{18}\text{O}_{\text{VSMOW}}$ of -3.8‰ . This $\delta^{18}\text{O}$ ratio is nearly identical to the early groundwater $\delta^{18}\text{O}_{\text{VSMOW}}$ of -4.4‰ (Adams and Diamond, 2017). It follows that the lack of dissolved organic carbon, the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the low $\delta^{18}\text{O}$ of HMD reflect the properties of end-member groundwaters from the Vindelician High. The recrystallization implies that groundwater continued to flow through the Upper Muschelkalk following matrix dolomitization.

Several lines of evidence indicate that these flowing groundwaters eventually dedolomitized the TMD and HMD. Dedolomitization is generally attributed to either fluids that have interacted with evaporites or to oxidation of ferroan dolomites during sub-aerial exposure (Vandeginste & John, 2012). Since the Hauptmuschelkalk was not subaerially exposed following dolomitization, the dedolomitization must be due to sulphate-enriched fluids. It follows that the likeliest dedolomitizing fluids were the same sulphate-enriched groundwaters that recrystallized the HMD, based on the coinciding stratigraphic occurrence of HMD and dedolomitization, the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of the one dedolomitized bed that matches the values of HMD around it, and the sulphate-enriched and Ca-enriched character of the groundwaters. Once reflux ceased, or decreased, the groundwaters would have lost their incoming source of magnesium and the groundwaters would have returned to dolomite undersaturation, thereby dedolomitizing the HMD and lower Trigonodus Dolomit.

In this study, the proposed model of infiltration of hypersaline brines into groundwater accounts for the observed stable and strontium isotopes, geochemistry, petrography and spatial and stratigraphic distributions of the matrix dolomites in the Swiss Trigonodus Dolomit. There are nonetheless implicit uncertainties associated with our choice of isotope fractionation factors, distribution coefficients, palaeotemperatures, end-member water compositions and the effects of possible later diagenesis. However, the values of these parameters used in this study's model are not extreme and therefore the resulting geochemical trends are likely robust.

6 Conclusions

The Middle Triassic Trigonodus Dolomit of Switzerland formed within an extensive homoclinal carbonate ramp along the southern Central European Basin. The unit records multiple sea-level fluctuations, along with a stratigraphically upwards increase in aridity and evaporative textures. Lettenkohle sediments lying directly above the Trigonodus Dolomit further indicate an environmental transition via numerous evaporite–brackish/terrestrial alternations. The observed geochemical and isotopic signatures of the Trigonodus Dolomit ultimately resulted from the juxtaposition of these two environments.

Petrographic and spatial evidence suggests that dolomitization occurred due to density-driven seepage-reflux of hypersaline evaporative brines. In apparent contradiction to this, geochemical and isotopic evidence indicates a strong influence of ^{87}Sr -enriched groundwaters. Previous authors have attributed the ^{87}Sr signal to later recrystallization but the new data presented in this study, which show a uniform, vertical $^{87}\text{Sr}/^{86}\text{Sr}$ trend at the regional scale, argues against this explanation. Instead, the strontium and oxygen isotopes indicate that dolomite formed upon gradual mixing of hypersaline brines into saline Mg-bearing groundwater that already had low $\delta^{18}\text{O}$ and high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. In view of the near-constant thickness of the Trigonodus Dolomit across the Swiss segment of the basin, it can be concluded that horizontal advection of the groundwater merged individual brine plumes and

allowed dolomitization to proceed in a stratified mixing column. The Hauptmuschelkalk dolomites resulted from the recrystallization of Trigonodus Matrix Dolomites in advecting groundwater following the brine reflux. Both dolomite populations demonstrate that the geochemical and isotopic signatures of early pre-dolomitization groundwaters can be preserved during seepage-reflux dolomitization.

Through the coupling of multiple petrographic, geochemical and isotopic signatures, the diagenetic evolution of the Swiss Trigonodus Dolomit has been reconstructed in detail. Future studies of the Upper Triassic in the wider Central European Basin should test for the numerous aforementioned trends, in order to establish the dolomitization history over the entire basin. It remains to be seen if other seepage-reflux dolomites display similar isotopic trends or if these trends are unique to the Swiss Trigonodus Dolomit.

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References

- Adams, A., & Diamond, L.W. (2017). Early diagenesis driven by widespread meteoric infiltration of a Central European carbonate ramp: a reinterpretation of the Upper Muschelkalk. *Sedimentary Geology*, 362, 37–52.
- Aigner, T. (1982). Calcareous tempestites: storm dominated stratification in Upper Muschelkalk Limestones (Middle Trias, SW Germany). In G. Einsele & A. Seilacher (Eds.), *Cyclic and Event Stratification* (pp. 180–198). Berlin: Springer-Verlag.
- Aigner, T. (1985). *Storm depositional systems. Dynamic stratigraphy in modern and ancient shallow marine sequences*. Berlin: Springer-Verlag.
- Aigner, T., & Bachmann, G.H. (1992). Sequence-stratigraphic framework of the German Triassic. *Sedimentary Geology*, 80, 115–135.
- Allan, J.R., & Matthews, R.K. (1977). Carbon and oxygen isotopes as diagenetic and stratigraphic tools: Surface and subsurface data, Barbados, West Indies. *Geology*, 5, 16–20.
- Allan, J.R., & Matthews, R.K. (1982). Isotope signatures associated with early meteoric diagenesis. *Sedimentology*, 29, 797–817.

-
- Alesi, J.E. (1984). Der Trigonodus-Dolomit im Oberen Muschelkalk von SW-Deutschland. *Arbeiten aus dem Institut für Geologie und Paläontologie an der Universität Stuttgart*, 79, 1–53.
- Aschwanden, L., Diamond, L.W., Adams, A., & Mazurek, M. (2017). Anhydrite-dissolution porosity in the Upper Muschelkalk carbonate aquifer, NE-Switzerland: implications for geothermal energy and geological storage of gas. *Procedia Earth and Planetary Science*, 17, 897–900.
- Baker, P.A., & Burns, S.J. (1985). Occurrence and formation of dolomite in organic-rich continental margin sediments. *AAPG Bulletin*, 69, 1917–1930.
- Baltzer, F., Kenig, F., Boichard, R., Plaziat, J.C., & Purser, B.H. (1994). Organic matter distribution, water circulation and dolomitization beneath the Abu Dhabi Sabkha (United Arab Emirates). In: B. Purser, M. Tucker, & D. Zenger (Eds.), *Dolomites: A Volume in Honour of Dolomieu Special Publications of the International Association of Sedimentologists* 21, (pp. 409–427). Oxford: Blackwell Scientific Publications.
- Banner, J.L., & Hanson, G.N. (1990). Calculation of simultaneous isotopic and trace element variations during water–rock interaction with applications to carbonate diagenesis. *Geochimica et Cosmochimica Acta*, 54, 3123–3137.
- Banner, J.L. (1995). Application of the trace element and isotope geochemistry of strontium to studies of carbonate diagenesis. *Sedimentology*, 42, 805–824.
- Bein, A., & Land, L.S. (1983). Carbonate sedimentation and diagenesis associated with Mg-Ca-Cl brines: the Permian San Andres Formation in the Texas Panhandle. *Journal of Sedimentary Petrology*, 53, 243–260.
- Bitterli, T., Graf, H.R., Matousek, F., & Wanner, M. (2000). *Erläuterungen zum Geologischen Atlas der Schweiz 1:25'000, Blatt Zurzach (LK 1050)*. Bern: Federal Office of Topography.
- Bodnar, R.J. (1993). Revised equation and table for determining the freezing point depression of H₂O–NaCl solutions. *Geochimica et Cosmochimica Acta*, 57, 683–684.
- Büchi, U.P., Lemcke, K., Wiener, G., & Zimdars, J. (1965). Geologische Ergebnisse der Erdölexploration auf das Mesozoikum im Untergrund des schweizerischen Molassebeckens. *Bulletin der Vereinigung Schweizerischer Petroleum-Geologen und –Ingenieure*, 32, 7–28.
- Budd, D.A. (1997). Cenozoic dolomites of carbonate islands: their attributes and origin. *Earth Science Reviews*, 42, 1–47.
- Bühl, H., & Bollinger, N. (1999). Die Grundwasserbohrung Trasadingen. *Bulletin für angewandte Geologie*, 4, 129–139.
- Butler, G.P. (1969). Modern evaporite deposition and geochemistry of coexisting brines, the sabkha, Trucial Coast, Arabian Gulf. *Journal of Sedimentary Petrology*, 39, 70–89.
- Chevalier, G., Diamond, L.W., & Leu, W. (2010). Potential for deep geological sequestration of CO₂ in Switzerland: a first appraisal. *Swiss Journal of Geosciences*, 103, 427–455.
- Clark, I. (2015). *Groundwater Geochemistry and Isotopes*. Boca Raton: CRC Press.
- Clauser, C., Hartmann, A., Koch, A., Mottaghy, D., Pechinig, R., & Rath, V. (2007). *Erstellung statistisch abgesicherter thermischer und hydraulischer Gesteinseigenschaften für den flachen und tiefen Untergrund in Deutschland, Phase 1—Westliche Molasse und nördlich*
-

-
- angrenzendes Süddeutsches Schichtstufenland* (Final report for BMU-project FKZ 0329985). Aachen: RWTH Aachen University.
- De Haller, A., Mazurek, M., Spangenberg, J., & Möri, A. (2014). *SF (Self-sealing of faults and paleo-fluid flow): Final report*. Wabern: Federal Office of Topography.
- Deutsche Stratigraphische Kommission (2002). *Stratigraphische Tabelle von Deutschland 2002*. Potsdam: Geoforschungs Zentrum.
- Diamond, L.W. (2003). Systematics of H₂O inclusions. In: I.M. Samson, A.J. Anderson, & D.D. Marshall (Eds.), *Fluid Inclusions: Analysis and Interpretation, Mineralogical Association of Canada Short Course 32* (pp. 55–79). Ottawa: Mineralogical Association of Canada
- Diamond, L.W., Aschwanden, L., Mazurek, M., Wersin, P., Caldas, R., Adams, ... Madonna, C. (2013). *Reservoir properties of the Upper Muschelkalk drill core at Schlattingen, NE Swiss Molasse Basin. A Combined Petrographic, Sedimentological, Geochemical and Petrophysical Study* (Unpublished report). Bern: Institute of Geological Sciences.
- Dickson, J.A.D. (1966). Carbonate identification and genesis as revealed by staining. *Journal of Sedimentary Petrology*, 36, 491–505.
- Diebold, P., Bitterli-Brunner, P., & Naef, H. (2006). *Erläuterungen zum Geologischen Atlas der Schweiz 1:25'000, Blatt Frick – Laufenburg (LK 1049, 1069)*. Wabern: Bundesamt für Landestopografie Swisstopo.
- Disler, C. (1914). *Stratigraphischer Führer durch die geologischen Formationen im Gebiet zwischen Aare, Birs und Rhein*. Basel: B. Wepf & Co.
- Dravis, J.J., & Yurewicz, D.A. (1985). Enhanced carbonate petrography using fluorescence microscopy. *Journal of Sedimentary Petrology*, 55, 795–804.
- Faure, G., & Powell, J.L. (1972). *Strontium Isotope Geology*. Berlin: Springer-Verlag, Berlin..
- Fischer, H., & Luterbacher, H. (1963). Das Mesozoikum der Bohrungen Courtion 1 (Kt. Fribourg) und Altishofen 1 (Kt. Luzern). *Beiträge zur Geologischen Karte der Schweiz, Neue Folge*, 115, 1–40.
- Franz, M., Henniger, M., & Barnasch, J. (2013). The strong diachronous Muschelkalk/Keuper facies shift in the Central European Basin: implications from the type-section of the Erfurt Formation (Lower Keuper, Triassic) and basin-wide correlations. *International Journal of Earth Sciences*, 102, 761–780.
- Franz, M., Kaiser, S.I., Fischer, J., Heunisch, C., Kustatscher, E., Luppold, F.W., Berner, U. & Röhling, H.-G. (2015). Eustatic and climatic control on the Upper Muschelkalk Sea (late Anisian/Ladinian) in the Central European Basin. *Global and Planetary Change*, 135, 1–27.
- Gaswirth, S.B., Budd, D.A., & Farmer, G.L. (2007). The role and impact of freshwater-seawater mixing zones in the maturation of regional dolomite bodies within the proto Floridan Aquifer, USA. *Sedimentology*, 54, 1065–1091.
- Geyer, O.F., & Gwinner, M.P. (2011). *Geologie von Baden-Württemberg*. Stuttgart: Schweizerbart.
- Gieskes, J.M., Elderfield, H., & Palmer, M.R. (1986). Strontium and its isotopic composition in interstitial waters of marine carbonate sediments. *Earth and Planetary Science Letters*, 77, 229–235.
-

-
- Gill, I.P., Moore, C.H., & Aharon, P. (1995). Evaporitic mixed-water dolomitization on St. Croix, U.S.V.I. *Journal of Sedimentary Research*, 65, 591–604.
- Guillong, M., Meier, D.L., Allan, M.M., Heinrich, C.A., & Yardley, B.W.D. (2006). Appendix A6: SILLS: A Matlab-based program for the reduction of laser ablation ICP-MS data of homogeneous materials and inclusions. *Mineralogical Association of Canada Short Course* 40, 328–333.
- Hagdorn, H., & Nitsch, E. (2009). *Field Guide, 6th International Triassic field workshop, September 7–11, 2009*. Tübingen.
- Hardie, L.A. (1987). Dolomitization: a critical view of some current views. *J. Sed. Petrol.*, 57, 166–183.
- Häring, M.O. (2001). *Technischer Bericht Geothermie-Sondierbohrung Otterbach 2, Basel*. Basel: Geothermal Explorers Ltd.
- Hauber, L. (1971). Zur Geologie des Salzfeldes Schweizerhalle–Zinggibrunn (Kt. Baselland). *Eclogae Geologicae Helveticae*, 64, 163–183.
- Hofmann, F. (1981). *Erläuterungen zum Geologischen Atlas der Schweiz 1:25'000, Blatt Neunkirch (LK 1031)*. Schweizerischen Geologischen Kommission.
- Hsü, K.J., & Siegenthaler, C. (1969). Preliminary experiments on hydrodynamic movement induced by evaporation and their bearing on the dolomite problem. *Sedimentology*, 12, 11–25.
- Jacobson, G., Jankowski, J., & Abell, R.S. (1991). Groundwater and surface water interaction at Lake George, New South Wales. *Journal of Australia Geology & Geophysics*, 12, 161–190.
- Jones, G.D., Whitaker, F.F., Smart, P.L., & Sanford, W.E. (2002). Fate of reflux brines in carbonate platforms. *Geology*, 30, 371–374.
- Jones, G.D., & Xiao, Y. (2005). Dolomitization, anhydrite cementation, and porosity evolution in a reflux system: Insights from reactive transport models. *AAPG Bulletin*, 89, 577–601.
- Kämpfe, C. (1984). Tiefbohrungen in Baden-Württemberg und umgebenden Ländern. *Arbeiten aus dem Institut für Geologie und Paläontologie an der Universität Stuttgart*, 80, 1–313.
- Kiefer, L.M. (2013). Permeable Muschelbänke im Oberen Muschelkalk des Schweizer Mittellandes – Ist eine geothermische Nutzung möglich? (Master thesis). Zürich: ETH Zürich.
- Koehrer, B.S., Heymann, C., Prousa, F., & Aigner, T. (2010). Multiple-scale facies and reservoir quality variations within a dolomite body — outcrop analog study from the Middle Triassic, SW German Basin. *Marine and Petroleum Geology*, 27, 386–411.
- Korte, C., Kozur, H.W., Bruckschen, P., & Veizer, J. (2003). Strontium isotope evolution of Late Permian and Triassic seawater. *Geochimica et Cosmochimica Acta*, 67, 47–62.
- Kozur, H. (1974). Biostratigraphie der germanischen Mitteltrias. Part 1: *Freiberger Forschungshefte C*, 280/1, 1–56. Part 2: *Freiberger Forschungshefte C*, 280/2, 1–71.
- Kupecz, J.A., Montanez, I.P., & Gao, G. (1993). Recrystallization of dolomite with time. In: R. Rezak, & D. Lavoie (Eds.), *Carbonate Microfabrics. Frontiers in Sedimentology* (pp. 187–193). New York: Springer-Verlag.
-

-
- Kupecz, J.A., & Land, L.S. (1994). Progressive recrystallization and stabilization of early-stage dolomite: Lower Ordovician Ellenburger Group, west Texas. In: B. Purser, M. Tucker, & D. Zenger (Eds.), *Dolomites: A Volume in Honour of Dolomieu, Special Publications of the International Association of Sedimentologists 21* (pp. 255–279). Oxford: Blackwell Scientific Publications.
- Land, L.S., Salem, M.R.I., & Morrow, D.W. (1975). Paleohydrology of ancient dolomites: geochemical evidence. *AAPG Bulletin*, 59, 1602–1625.
- Land, L.S. (1980). The isotopic and trace element geochemistry of dolomite: the state of the art. In: D.H. Zenger, J.B. Dunham, and R.L. Ethington (Eds.), *Concepts and Models of Dolomitization SEPM Spec. Publ. 28* (pp. 87–110). Tulsa: Society of Economic Paleontologists and Mineralogists.
- Land, L.S. (1991). Dolomitization of the Hope Gate Formation (north Jamaica) by seawater: Reassessment of mixing-zone dolomite. In: H.P. Taylor Jr., J.R. O’Neil, and I.R. Kaplan (Eds.), *Stable Isotope Geochemistry: A Tribute to Samuel Epstein. The Geochemical Society, Special Publication 3* (pp. 121–130). San Antonio: Geochemical Society.
- Ledermann, H. (1981). Geologie der Region Solothurn und Führer zum Geologischen Wanderweg über die Weissensteinkette. *Mitteilungen der Naturforschenden Gesellschaft des Kantons Solothurn*, 30, 1–87.
- Lemcke, K., & Wagner, R. (1961). Zur Kenntnis des vortertiären Untergrundes im Bodenseegebiet. *Bulletin der Vereinigung Schweizerischer Petroleum-Geologen und –Ingenieure*, 27, 9–14.
- Machel, H.G. (1988). Fluid flow direction during dolomite formation as deduced from trace-element trends. In: V. Shukla, & P.A. Baker (Eds.), *Sedimentology and Geochemistry of Dolostones. SEPM Special Publication 43* (pp. 115–125). Tulsa: Society of Economic Paleontologists and Mineralogists.
- Machel, H.G. (2004). Concepts and models of dolomitization: a critical reappraisal. In: C.J.R. Braithwaite, G. Rizzi, & G. Darke (Eds.), *The Geometry and Petrogenesis of Dolomite Hydrocarbon Reservoirs. Geological Society of London Special Publication 235* (pp. 7–63). London: The Geological Society.
- Machel, H.G., & Mountjoy, E.W. (1986). Chemistry and environments of dolomitization – a reappraisal. *Earth-Science Reviews*, 23, 175–222.
- Matter, A., Peters, Tj., Isenschmid, Ch., Bläsi, H.-R., & Ziegler, H.-J. (1987). Sondierbohrung Riniken. Nagra Technischer Bericht 86-02. Baden: Nagra.
- Matter, A., Peters, Tj., Bläsi, H.-R., Meyer, J., Ischi, H., & Meyer, Ch. (1988a). Sondierbohrung Weiach. Nagra Technischer Bericht 86-01. Baden: Nagra.
- Matter, A., Peters, Tj., Bläsi, H.-R., Schenker, F., & Weiss, H.-P. (1988b). Sondierbohrung Schafisheim. Technischer Bericht 86-03. Baden: Nagra.
- Mazurek, M., Hurford, A.J., & Leu, W. (2006). Unravelling the multi-stage burial history of the Swiss Molasse basin: integration of apatite fission track, vitrinite reflectance and biomarker isomerisation analysis. *Basin Research*, 18, 27–50.
- McKenzie, J.A., Hsü, K.J., & Schneider, J.F. (1980). Movement of subsurface waters under the sabkha, Abu Dhabi, UAE, and its relation to evaporative dolomite genesis. In: D.H. Zenger,
-

-
- J.B. Dunham, and R.L. Ethington (Eds.), Concepts and Models of Dolomitization *SEPM Spec. Publ.* 28 (pp. 11–30). Tulsa: Society of Economic Paleontologists and Mineralogists.
- McKenzie, J.A. (1981). Holocene dolomitization of calcium carbonate sediments from the coastal sabkhas of Abu Dhabi, U.A.E.: a stable isotope study. *Journal of Geology*, 89, 185–198.
- Melim, L.A., & Scholle, P.A. (2002). Dolomitization of the Capitan Formation forereef facies (Permian, west Texas and New Mexico): seepage reflux revisited. *Sedimentology*, 49, 1207–1227.
- Merki, P. (1961). Der Obere Muschelkalk im östlichen Schweizer Jura. *Eclogae Geologicae Helvetiae*, 54, 137–220.
- Meyers, W.J., Lu, F.H., & Zachariah, J.K. (1997). Dolomitization by mixed evaporative brines and freshwater, Upper Miocene carbonates, Nijar Spain. *Journal of Sedimentary Research*, 67, 898–912.
- Muir, M., Lock, D., & von der Borch, C. (1980). The Coorong Model for penecontemporaneous dolomite formation in the Middle Proterozoic McArthur Group, Northern Territory, Australia. In: D.H. Zenger, J.B. Dunham, and R.L. Ethington (Eds.), Concepts and Models of Dolomitization *SEPM Spec. Publ.* 28 (pp. 51–68). Tulsa: Society of Economic Paleontologists and Mineralogists.
- Müller, D.W., McKenzie, J.A., & Mueller, P.A. (1990). Abu Dhabi sabkha, Persian Gulf, revisited: Application of strontium isotopes to test an early dolomitization model. *Geology*, 18, 618–621.
- Nagra (1984). *Die Kernbohrung Beznau. Nagra Technischer Bericht NTB 84-34*. Baden: Nagra.
- Nagra (1985). *Sondierbohrung Böttstein Untersuchungsbericht. Nagra Technischer Bericht 85-01*. Baden: Nagra.
- Nagra (1992). *Sondierbohrung Siblingen Untersuchungsbericht. Nagra Technischer Bericht 90-34*. Baden: Nagra.
- Nagra (2001). *Sondierbohrung Benken - Untersuchungsbericht. Nagra Technischer Bericht NTB 00-01*. Baden: Nagra.
- NEFF (1980). *Forschungsprojekt Geothermische Energie und unterirdische Wärmespeicherung: Teilprojekt I: Geothermische Prospektion im Raume Koblenz–Wildegge-Dielsdorf (Schlussbericht)*. Basel: Nationaler Energie-Forschungs-Fonds.
- Oostrom, M., Dane, J.H., Güven, O., & Hayworth, J.S. (1992). Experimental investigation of dense solute plumes in an unconfined aquifer model. *Water Resources Research*, 28, 2315–2326.
- Pal, M., Taberner, C., & Tueckmantel, C. (2014). Simulation of end-member scenarios of density-driven flow: prediction of dolostone geobody dimensions using COMSOL. In: S.M. Agar, & S. Geiger (Eds.), *Fundamental Controls on Fluid Flow in Carbonates: Current Workflows to Emerging Technologies. Geological Society London Special Publications 406* (pp. 209–228). London: The Geological Society.
- Parrish, J.T. (1993). Climate of the supercontinent Pangea. *The Journal of Geology*, 101, 215–233.
-

-
- Pearson Jr., F.J., Balderer, W., Loosli, H.H., Lehmann, B.E., Matter, A., Peters, T., Schmassmann, H., & Gautschi, A. (1991). *Applied Isotope Hydrogeology – A Case Study in Northern Switzerland*. Amsterdam: Elsevier Scientific Publishers.
- Pietsch, J.S., Wetzel, A., & Jordan, P. (2016). A new lithostratigraphic scheme for the Schinznach Formation (upper part of the Muschelkalk Group of northern Switzerland). *Swiss Journal of Geosciences*, 109, 285–307.
- Pingitore, N.E. (1982). The role of diffusion during carbonate diagenesis. *J. Sed. Petrol.*, 52, 27–39.
- Pöppelreiter, M., & Aigner, T. (2003). Unconventional pattern of reservoir facies distribution in epeiric successions: Lessons from an outcrop analog (Lower Keuper, Germany). *AAPG Bulletin*, 87, 39–70.
- Pöppelreiter, M., & Aigner, T. (2008). High-resolution sequence stratigraphy, facies patterns and controls in a mixed epeiric shelf: implications for reservoir prediction (Lower Keuper, Triassic, German Basin). In: B.R. Pratt, & C. Holmden (Eds.), *Dynamics of Epeiric Seas. Geological Association of Canada Special Paper 48* (pp. 283–301). St. John's: Geological Association of Canada.
- Ramseyer, K., Miano, T.M., D'Orazio, V., Wildberger, A., Wagner, T., & Geister, J. (1997). Nature and origin of organic matter in carbonates from speleothems, marine cements and coral skeletons. *Organic Geochemistry*, 26, 361–378.
- Ramseyer, K., Fischer, J., Matter, A., Eberhardt, P., & Geiss, J. (1989). A cathodoluminescence microscope for low intensity luminescence. *Journal of Sedimentary Research*, 59, 619–622.
- R Core Team (2015). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. Retrieved from <https://www.R-project.org/>.
- Reif, W.E. (1982). Muschelkalk/Keuper Bone-Beds (Middle Triassic, SW-Germany) – Storm condensation in a regressive cycle. In G. Einsele & A. Seilacher (Eds.), *Cyclic and Event Stratification* (pp. 300–325). Berlin: Springer-Verlag.
- Reinhold, C. (1997). Multiple episodes of dolomitization and dolomite recrystallization during shallow burial in Upper Jurassic shelf carbonates: eastern Swabian Alb, southern Germany. *Sedimentary Geology*, 121, 71–95.
- Rogowski, E., & Simon, T. (2005). Salzerkundungsbohrung Stetten (Zollernalbkreis, Baden-Württemberg). *Landesamt für Geologie, Rohstoffe und Bergbau Informationen*, 17, 136–150.
- Rosenbaum, J., & Sheppard, S.M.F. (1986). An isotopic study of siderites, dolomites and ankerites at high temperatures. *Geochimica et Cosmochimica Acta*, 50, 1147–1150.
- Sachs, O., & Eberhard, M. (2012). *Grundlagenstudie zur Erstellung einer geotechnischen Wegleitung für EWS Bohrungen mit potenziell gips- und anhydrithaltigen Gesteinen – geophysikalische und mineralogische Untersuchungen an drei oberflächennahen Bohrungen in sulfathaltigen Keupergesteinen*. Bern: Bundesamt für Energie BFE.
- Schauer, M., & Aigner, T. (1997). Cycle stacking pattern, diagenesis and reservoir geology of peritidal dolostones, Trigonodus-Dolomite, Upper Muschelkalk (Middle Triassic, SW-Germany). *Facies*, 37, 99–114.
- Schmidt, C., Braun, L., Paltzer, G., Muhlberg, M., Chirst, P., & Jacob, F. (1924). *Die Bohrungen von Buix bei Pruntrut und Allschwil bei Basel*. Bern: Geograph Kartenverlag.
-

-
- Sibley, D.F., & Gregg, J.M. (1987). Classification of dolomite rock textures. *Journal of Sedimentary Research*, 57, 967–975.
- Sibley, D.F., Nordeng, S.H., & Borkowskim, M.L. (1994). Dolomitization kinetics in hydrothermal bombs and natural settings. *Journal of Sedimentary Research*, 3, 630–637.
- Simmons, C.T., Narayan, K.A., & Wooding, R.A. (1999). On a test case for density-dependent groundwater flow and solute transport models: The salt lake problem. *Water Resources Research*, 35, 3607–3620.
- Sommaruga, A., Eichenberger, U., & Marillier, F. (2012). *Seismic atlas of the Swiss Molasse Basin*. Wabern: Federal Office of Topography Swisstopo.
- Stampfli, G.M., & Borel, G.D. (2002). A plate tectonic model for the Paleozoic and Mesozoic constrained by dynamic plate boundaries and restored synthetic oceanic isochrones. *Earth and Planetary Science Letters*, 196, 17–33.
- Tucker, M.E., & Wright, V.P. (1990). *Carbonate Sedimentology*. Oxford: Blackwell Scientific Publications.
- Tucker, M.E., & Marshall, J. (2004). Diagenesis and geochemistry of Upper Muschelkalk (Triassic) buildups and associated facies in Catalonia (NE Spain): a paper dedicated to Francesc Calvet. *Geologic Acta*, 2, 257–269.
- Turpin, M., Nader, F.H., & Kohler, E. (2012) Empirical calibration for dolomite stoichiometry calculation: Application on Triassic Muschelkalk-Lettenkohle carbonates (French Jura). *Oil & Gas Science and Technology – Rev. IFP Energies nouvelles*, 67, 77–95.
- Ufrecht, W., & Hölzl, S. (2006). Salinare Mineral- und Thermalwässer im Oberen Muschelkalk (Trias) im Großraum Stuttgart – Rückschlüsse auf Herkunft und Entstehung mit Hilfe der $^{87}\text{Sr}/^{86}\text{Sr}$ -Strontium-Isotopie. *Zeitschrift der Deutschen Gesellschaft für Geowissenschaften*, 157, 299–315.
- Vahrenkamp, V.C., & Swart, P.K. (1990). New distribution coefficient for the incorporation of strontium into dolomite and its implications for the formation of ancient dolomites. *Geology*, 18, 387–391.
- Van Dam, R.L., Eustice, B.P., Hyndman, D.W., Wood, W.W. and Simmons, C.T. (2014) Electrical imaging and fluid modelling of convective fingering in a shallow water-table aquifer. *Water Resources Research*, 50, 954–968.
- Vandeginste, V., & John, C.M. (2012). Influence of climate and dolomite composition on dedolomitization: insights from a multi-proxy study in the Central Oman Mountains. *Journal of Sedimentary Research*, 82, 177–195.
- Vasconcelos, C., McKenzie, J.A., Warthmann, R., & Bernasconi, S.M. (2005) Calibration of the $\delta^{18}\text{O}$ paleothermometer for dolomite precipitated in microbial cultures and natural environments. *Geology*, 33, 317–320.
- Vecsei, A. (1998). A sandy tidal coast in the uppermost Muschelkalk and the origin of the Muschelkalk/Keuper boundary in the southwestern Germanic basin. *Geologische Rundschau*, 86, 835–851.
- Vollmayr, T. (1971). Zur Geologie des Feldes Pfullendorf-Ostrach. *Bulletin der Vereinigung Schweizerischer Petroleum-Geologen und –Ingenieure*, 32, 7–38.
-

-
- Wagner, G. (1913). Beiträge zur Stratigraphie und Bildungsgeschichte des Oberen Hauptmuschelkalks und der unteren Lettenkohle in Franken. *Geologische und Paläontologische Abhandlungen*, 12, 1–180.
- Wahlman, G.P. (2010). Reflux dolomite crystal size variation in cyclic inner ramp reservoir facies, Bromide Formation (Ordovician), Arkoma Basin, southeastern Oklahoma. *The Sedimentary Record*, 8, 4–9.
- Wanless, H.R. (1979). Limestone response to stress: pressure solution and dolomitization. *Journal of Sedimentary Petrology*, 49, 437–462.
- Warren, J.K. (2000). Dolomite: Occurrence, Evolution and Economically Important Associations. *Earth-Science Reviews*, 52, 1–81.
- Wood, W.W., Sanford, W.E., & Al Habshi, A.R.S. (2002). Source of solutes to the coastal sabkha of Abu Dhabi. *Geological Society of America Bulletin*, 114, 259–268.
- Wood, W.W., Sanford, W.E., & Frape, S.K. (2005). Chemical openness and potential for misinterpretation of the solute environment of coastal sabkhat. *Chemical Geology*, 215, 361–372.
- Wooding, R.A., Tyler, S.C., & White, I. (1997). Convection in groundwater below an evaporating salt lake: 1. Onset of instability. *Water Resources Research*, 33, 1199–1217.
- Yechieli, Y., & Wood, W.W. (2002) Hydrogeologic processes in saline systems: playas, sabkhas, and saline lakes. *Earth-Science Reviews*, 58, 343–365.
- Zehe, S., & Geng, A. (2001). Origin and diagenesis of dolomite from the Muschelkalk Group (Middle Triassic) of SW Germany. *Neues Jahrbuch für Geologie und Paläontologie Abhandlungen*, 221, 359–395.
- Zenger, D.H., Dunham, J.B., & Ethington, R.L. (1980). *Concepts and Models of Dolomitization*. *SEPM Special Publication 28*. Tulsa: Society of Economic Paleontologists and Mineralogists.
- Ziegler, P.A. (1990) *Geological Atlas of Western and Central Europe, 2nd edn*. The Hague: Shell Internationale Petroleum Maatschappij.

Appendix

Table A3.1. List of boreholes used for kriging interpolation.

Borehole name	CH1903+		Dolomite fraction (%) ¹	UMK thickness (m) ²	HMK thickness (m) ²	TD thickness (m) ²	Reference
	E	N					
Altishofen	2640375	1228130	58	48	20	28	Fischer and Luterbacher (1963)
Aouze	2484980	1360255	0	46	46	0	BRGM
Argilly 1	2414990	1214824	100	18	0	18	BRGM
B-06	2722400	1301056	41	68	40	28	Clauser et al. (2007)
B-07	2755300	1305606	58	57	24	33	Clauser et al. (2007)
B-13	2747640	1301613	31	62	43	19	Clauser et al. (2007)
B-15	2759850	1309764	45	49	27	22	Clauser et al. (2007)
B-16	2738480	1285107	50	50	25	25	Clauser et al. (2007)
Bad Schinznach-S3	2654769	1256187	46	87	47	40	Diebold et al. (2006)
Bellemagny 1	2572988	1282066	19	73	59	14	BRGM
Benken	2690989	1277843	59	63	26	37	NAGRA (2001)
Berlingen	2719685	1280195	18	66	54	12	Büchi et al. (1965)
Beznau	2659491	1267242	49	71	37	35	NAGRA (1984)
Bienville 1	2425710	1382226	100	37	0	37	BRGM
Binnenweg 1	2616594	1365696	0	75	75	0	BRGM
Blinfey 1	2410772	1353585	100	28	0	28	BRGM
Bonlieu 1	2479143	1161130	0	31	31	0	BRGM
Böttstein	2659341	1268556	39	75	46	29	NAGRA (1985)
Bözberg	2651809	1256627	48	77	40	37	This Study
Bresse Nord 101	2432532	1179500	100	23	0	23	BRGM
Bresse Sud 2	2430080	1096076	100	6	0	6	BRGM
Briod 103	2460433	1169777	38	40	25	15	BRGM
Buez	2522418	1235845	17	60	50	10	BRGM
Buix	2568782	1258620	28	71	51	20	Schmidt et al. (1924)
Champvans 1	2485490	1233256	32	56	38	18	BRGM
Chatelblanc 1	2498122	1170589	20	65	52	13	BRGM
Chevillon 1	2429943	1378810	100	38	0	38	BRGM
Chevraumont 1	2481930	1373194	18	68	56	13	BRGM
Cordonnet 1	2490026	1255402	55	51	23	28	BRGM
Courtion	2572410	1189420	32	53	36	17	Fischer and Luterbacher (1963)
Crançot	2461963	1172018	44	40	23	18	BRGM
Densbüren-Asp	2646455	1255054	45	87	48	39	Diebold et al. (2006)
Dingelsdorf 1	2727953	1288463	31	67	46	21	Lemcke and Wagner (1961)
Domevre 1	2489631	1408893	9	58	53	5	BRGM
Droyes 1	2400958	1379151	100	27	0	27	BRGM
Embermenil 1	2544256	1386013	0	64	64	0	BRGM
Eternoz 1	2491324	1207261	26	57	42	15	BRGM
Frick 1	2643762	1263020	33	96	64	32	Sachs and Eberhard (2012)
Gendrey 1	2472146	1231028	30	58	40	18	BRGM
Gipf-Oberfrick	2642021	1261839	30	77	54	23	Diebold et al. (2006)
Hausen-Habsburg HH1	2657836	1256939	55	99	45	54	NEFF (1980)
Herdern	2711308	1274597	47	64	34	30	This Study
Illfurth R. 1	2587845	1281488	9	66	60	6	BRGM
Jura 115	2457185	1170825	0	26	26	0	BRGM

Knoeringue 1	2593562	1268879	13	54	47	7	BRGM
Kreuzlingen	2729201	1276169	14	65	56	9	Büchi et al. (1965)
Laveron 1	2503052	1180241	14	70	60	10	BRGM
Lezeville 1	2447786	1366221	100	46	0	46	BRGM
Lindau	2692815	1255098	61	61	24	37	This Study
Lipsheim 2	2615385	1371298	69	65	20	45	BRGM
M	2703083	1353379	26	82	61	21	Rogowski and Simon (2005)
Mackenheim 1	2610066	1336411	21	87	69	18	BRGM
Macornay 101	2455289	1168108	35	29	19	10	BRGM
Meistratzheim 2	2609335	1366932	25	74	55	19	BRGM
Mönchsrot 14	2791565	1321473	14	29	25	4	Kämpfe (1984)
Montbarrey 1	2467485	1205915	50	55	28	28	BRGM
Montbouton 1	2560903	1257706	31	71	49	22	BRGM
Montcoy 1	2413533	1183107	100	22	0	22	BRGM
Montier-en-Der 1	2405814	1373633	100	36	0	36	BRGM
Montrond-Le-Chateau 1	2494853	1221724	33	68	46	23	BRGM
Moutherot	2469766	1233907	13	48	42	6	BRGM
Muntzenheim 1	2602722	1327169	40	69	41	28	BRGM
Muttersholtz 1	2608642	1346301	21	63	50	13	BRGM
Obermarchtal 1	2760423	1343527	36	47	30	17	Kämpfe (1984)
Obermodern 1	2606473	1411018	0	71	71	0	BRGM
Oberroedern 101	2638389	1419269	0	55	55	0	BRGM
Oeschgen-S	2643762	1263020	31	70	48	22	Diebold et al. (2006)
Orny 1	2512643	1429958	0	54	54	0	BRGM
Orsan 1	2521639	1233312	0	49	49	0	BRGM
Otterbach 2	2612430	1269685	26	83	62	21	Häring (2001)
Pfaffnau 1	2632708	1231789	45	64	35	29	Büchi et al. (1965)
Pontailier 1	2447443	1241074	100	45	0	45	BRGM
Publy 101	2462967	1166590	28	36	26	10	BRGM
Riburg 17	2629175	1266490	34	74	49	25	Kämpfe (1984)
Riniken	2656604	1261780	50	73	37	36	Matter et al. (1987)
Ruckfeld 1	2662950	1266850	25	67	50	17	Bitterli et al. (2000)
Rudersberg	2752025	1417235	6	77	73	5	Kämpfe (1984)
Salzbohrung Frick Nr. 5	2644264	1261903	22	67	52	15	Diebold et al. (2006)
Schafisheim	2653620	1246760	44	59	33	26	Matter et al. (1988b)
Scheibenhard F 102	2649057	1424835	0	68	68	0	BRGM
Schlattingen	2699380	1281630	58	58	25	34	This Study
Schweighouse 2	2582704	1289973	0	47	47	0	BRGM
Schweighouse sur Moder 1D	2622272	1408353	0	67	67	0	BRGM
Siblingen	2680090	1286693	57	54	24	31	NAGRA (1992)
Sorneville 1	2526164	1397343	0	67	67	0	BRGM
St Jean de Losne 1	2437567	1220990	100	45	0	45	BRGM
Sulz	2649390	1264761	39	66	40	26	Diebold et al. (2006)
Trasadingen	2647231	1280264	31	62	43	19	Bühl and Bollinger (1999)
Upflamör 1	2746523	1341736	24	51	39	12	Kämpfe (1984)
Valempoulières 1	2480709	1186574	0	33	33	0	BRGM
Velesme 1	2467492	1253500	100	50	0	50	BRGM
Vellerot Les Belvoir 1	2536858	1245756	18	74	61	13	BRGM
Vevy 101	2462526	1169435	36	42	27	15	BRGM
Weiach	2676750	1268620	55	69	31	38	Matter et al. (1988)
Weissenstein-2	2606001	1234000	36	55	35	20	Ledermann (1981)

Wilchingen	2675730	1279740	22	67	52	15	Hofmann (1981)
Zurzach Acheberg L3	2663023	1270585	25	67	50	17	Bitterli et al. (2000)
Zurzach Acheberg S2	2661686	1271113	29	59	42	17	Bitterli et al. (2000)
Triemli	2679620	1246890	48	56	29	27	Kiefer (2013)
Pfullendorf 3	2735509	1312451	52	67	32	35	Vollmayr (1971)
Zinggibrunn 18	2618330	1264355	29	52	37	15	Hauber (1971)
Zinggibrunn 32	2618000	1264070	25	72	54	18	Hauber (1971)
Zinggibrunn 34	2617350	1263220	24	68	52	16	Hauber (1971)
Zinggibrunn 49	2616938	1263354	28	75	54	21	Hauber (1971)
Zinggibrunn 50	2617038	1263098	22	66	51	15	Hauber (1971)
Zinggibrunn 59	2616754	1262873	23	64	49	15	Hauber (1971)
Zinggibrunn 33	2616570	1262460	37	79	50	29	Hauber (1971)
Zinggibrunn 54	2617930	1262110	20	77	61	16	Hauber (1971)
Zinggibrunn 55	2616120	1262130	32	64	44	20	Hauber (1971)
Zinggibrunn 56	2616247	1261596	35	65	42	22	Hauber (1971)

¹ Calculated by: TD-thickness / UMK-thickness × 100.

² UMK denotes Upper Muschelkalk; HMK denotes Hauptmuschelkalk; TD denotes Trigonodus Dolomit.

Table A3.2. Stable oxygen and carbon isotope analyses of matrix dolomites (TMD), dedolomite and Hauptmuschelkalk dolomites (HMD).

Borehole	Depth (m)	$\delta^{13}\text{C}$ ‰ (VPDB)	$\delta^{18}\text{O}$ ‰ (VPDB)	Height above HMK ¹ (m)	Depth below Lettenkohle (m)	Height above SS ² (m)	Sample
Schlattingen	1130.53	0.45	-4.31	15.00	18.53	46.22	TMD
Schlattingen	1132.34	0.59	-5.01	13.19	20.34	44.41	TMD
Schlattingen	1141.69	0.85	-5.68	3.84	29.69	35.06	TMD
Schlattingen	1144.62	1.01	-5.53	0.91	32.62	32.13	TMD
Schlattingen	1145.45	1.06	-6.33	0.08	33.45	31.30	Dedolomite
Schlattingen	1140.13	1.07	-4.84	5.40	28.13	36.62	TMD
Schlattingen	1121.87	-0.01	-2.94	23.66	9.87	54.88	TMD
Schlattingen	1126.48	1.06	-3.73	19.05	14.48	50.27	TMD
Schlattingen	1127.83	1.12	-4.24	17.70	15.83	48.92	TMD
Schlattingen	1135.58	0.33	-5.70	9.95	23.58	41.17	TMD
Benken	813.31	0.59	-3.49	35.16	1.96	73.02	TMD
Benken	816.16	0.73	-2.76	32.31	4.81	70.17	TMD
Benken	821.52	0.82	-5.35	26.95	10.17	64.81	TMD
Benken	822.00	0.70	-3.54	26.47	10.65	64.33	TMD
Benken	825.11	1.02	-2.61	23.36	13.76	61.22	TMD
Benken	836.46	0.71	-4.39	12.01	25.11	49.87	TMD
Benken	839.81	0.80	-4.39	8.66	28.46	46.52	TMD
Benken	840.10	0.86	-4.55	8.37	28.75	46.23	TMD
Benken	828.14	1.07	-3.79	20.33	16.79	58.19	TMD
Benken	848.63	1.33	-6.42	-0.16	37.28	37.70	TMD
Böttstein	122.65	-0.30	-2.79	28.18	1.66	81.95	TMD
Böttstein	126.55	0.52	-3.15	24.28	5.56	78.05	TMD
Böttstein	137.20	1.25	-3.59	13.63	16.21	67.40	TMD
Böttstein	138.15	1.08	-4.03	12.68	17.16	66.45	TMD
Böttstein	141.40	0.85	-4.05	9.43	20.41	63.20	TMD
Böttstein	149.10	0.85	-3.23	1.73	28.11	55.50	TMD
Bözberg	60.62	-0.04	-1.77	35.46	2.20	84.77	TMD
Bözberg	61.33	0.18	-2.61	34.75	2.91	84.06	TMD
Bözberg	64.14	0.98	-3.13	31.94	5.72	81.25	TMD
Bözberg	64.82	1.06	-3.20	31.26	6.40	80.57	TMD
Bözberg	71.40	0.62	-3.18	24.68	12.98	73.99	TMD
Bözberg	72.88	1.18	-3.31	23.20	14.46	72.51	TMD
Bözberg	75.82	0.87	-4.13	20.26	17.40	69.57	TMD
Bözberg	78.01	0.86	-3.88	18.07	19.59	67.38	TMD
Bözberg	81.92	0.86	-3.44	14.16	23.50	63.47	TMD
Bözberg	82.30	0.82	-3.82	13.78	23.88	63.09	TMD
Bözberg	83.06	0.91	-3.20	13.02	24.64	62.33	TMD
Bözberg	85.47	0.92	-3.38	10.61	27.05	59.92	TMD
Bözberg	86.20	1.04	-2.01	9.88	27.78	59.19	TMD
Bözberg	89.32	0.81	-2.75	6.76	30.90	56.07	TMD
Bözberg	94.66	1.10	-5.21	1.42	36.24	50.73	TMD
Bözberg	95.58	0.88	-6.72	0.50	37.16	49.81	TMD
Schafisheim	1230.80	0.85	-2.55	23.50	4.72	74.18	TMD
Schafisheim	1231.18	0.87	-1.05	23.12	5.10	73.80	TMD
Schafisheim	1231.47	0.48	-2.04	22.83	5.39	73.51	TMD
Schafisheim	1232.55	0.18	-3.10	21.75	6.47	72.43	TMD
Schafisheim	1233.76	0.66	-2.81	20.54	7.68	71.22	TMD
Schafisheim	1234.38	0.55	-2.60	19.92	8.30	70.60	TMD
Schafisheim	1233.93	0.65	-3.10	20.37	7.85	71.05	TMD

Schafisheim	1252.38	1.00	-6.28	1.92	26.30	52.60	TMD
Schafisheim	1252.77	1.09	-6.46	1.53	26.69	52.21	TMD
Schafisheim	1254.25	1.03	-6.49	0.05	28.17	50.73	TMD
Siblingen	191.09	0.87	-4.12	16.68	14.98	58.30	TMD
Siblingen	200.20	0.80	-4.46	7.57	24.09	49.19	TMD
Siblingen	180.36	0.24	-3.47	27.41	4.25	69.03	TMD
Siblingen	189.77	0.94	-3.98	18.00	13.66	59.62	TMD
Siblingen	177.75	0.27	-3.60	30.02	1.64	71.64	TMD
Siblingen	195.72	1.08	-4.98	12.05	19.61	53.67	TMD
Weiach	820.67	0.63	-3.64	36.38	2.11	76.99	TMD
Weiach	824.85	0.50	-3.31	32.20	6.29	72.81	TMD
Weiach	825.47	0.71	-3.74	31.58	6.91	72.19	TMD
Weiach	826.00	0.67	-4.19	31.05	7.44	71.66	TMD
Weiach	828.72	0.61	-3.40	28.33	10.16	68.94	TMD
Weiach	833.90	1.10	-3.20	23.15	15.34	63.76	TMD
Weiach	834.25	1.00	-3.63	22.80	15.69	63.41	TMD
Weiach	838.66	0.70	-4.11	18.39	20.10	59.00	TMD
Weiach	841.56	0.77	-4.89	15.49	23.00	56.10	TMD
Weiach	845.15	0.27	-4.44	11.90	26.59	52.51	TMD
Weiach	846.73	1.00	-4.42	10.32	28.17	50.93	TMD
Weiach	850.60	0.80	-4.19	6.45	32.04	47.06	TMD
Pfaffnau	1546.42	0.51	-3.44	28.58	2.76	61.45	TMD
Pfaffnau	1546.52	0.51	-2.91	28.48	2.86	61.35	TMD
Pfaffnau	1548.60	0.98	-4.01	26.40	4.94	59.27	TMD
Pfaffnau	1555.03	1.03	-4.38	19.97	11.37	52.84	TMD
Pfaffnau	1553.27	1.10	-4.03	21.73	9.61	54.60	TMD
Pfaffnau	1556.04	0.99	-4.11	18.96	12.38	51.83	TMD
Pfaffnau	1548.30	0.87	-3.38	26.70	4.64	59.57	TMD
Lindau	2228.65	0.37	-2.93	36.35	6.15	69.85	TMD
Lindau	2225.51	0.51	-3.83	39.49	3.01	72.99	TMD
Lindau	2230.25	0.57	-4.16	34.75	7.75	68.25	TMD
Lindau	2231.59	0.68	-4.23	33.41	9.09	66.91	TMD
Lindau	2256.71	0.82	-4.86	8.29	34.21	41.79	TMD
Lindau	2232.64	0.82	-3.38	32.36	10.14	65.86	TMD
Lindau	2227.24	0.82	-4.35	37.76	4.74	71.26	TMD
Lindau	2238.78	0.94	-3.48	26.22	16.28	59.72	TMD
Lindau	2233.25	0.96	-2.84	31.75	10.75	65.25	TMD
Lindau	2235.19	0.96	-3.48	29.81	12.69	63.31	TMD
Lindau	2259.12	1.00	-5.19	5.88	36.62	39.38	TMD
Lindau	2246.67	1.02	-5.03	18.33	24.17	51.83	TMD
Lindau	2261.45	1.21	-3.84	3.55	38.95	37.05	TMD
Lindau	2236.53	0.95	-4.26	28.47	14.03	61.97	TMD
Lindau	2244.98	0.77	-3.94	20.02	22.48	53.52	TMD
Lindau	2258.14	1.13	-5.69	6.86	35.64	40.36	TMD
Bözberg	108.40	1.49	-6.64	-12.32	49.98	36.99	HMD
Bözberg	117.89	1.73	-5.97	-21.81	59.47	27.50	HMD
Bözberg	121.95	1.99	-6.63	-25.87	63.53	23.44	HMD
Bözberg	98.52	1.12	-6.54	-2.44	40.10	46.87	HMD
Bözberg	94.66	0.98	-6.34	1.42	36.24	50.73	HMD

¹Hauptmuschelkalk

²Sulfatschichten.