

Geothermal Carbonate Scaling: Forensic Studies Applying High-Resolution Geochemical Methods

Ronny Boch¹, János Szanyi², Albrecht Leis³, Andrea Mindszenty⁴, József Deák⁵, Tobias Kluge⁶, Dorothee Hippler¹, Attila Demény⁷ and Martin Dietzel¹

¹Graz University of Technology, Institute of Applied Geosciences, Rechbauerstr. 12, 8010 Graz, Austria

²University of Szeged, Dept. of Mineralogy, Geochemistry & Petrology, Egyetem u. 2, 6722 Szeged, Hungary

³Joanneum Research, Resources – Inst. f. Water, Energy & Sustainability, Elisabethstr. 18, 8010, Graz, Austria

⁴Eötvös L. University, Dept. of Physical & Applied Geology, Pázmány P. sétány 1/c, 1117 Budapest, Hungary

⁵GWIS – Ground Water Isotope Studies Ltd., Hóvirág u. 9, 8200 Veszprém, Hungary

⁶University of Heidelberg, Inst. of Environmental Physics, Neuenheimer Feld 229, 69120 Heidelberg, Germany

⁷Hungarian Academy of Sciences, Inst. f. Geol. & Geochem. Research, Budaorsi ut 45, 1112 Budapest, Hungary

e-mail: ronny.boch@tugraz.at

Keywords: geothermal scaling, carbonate precipitates, environmental archive, crystal growth, Pannonian Basin, steel corrosion, heat exchanger clogging, microbial activity, geothermal energy

ABSTRACT

Exploitation of thermal water frequently entails the precipitation of various minerals (scaling) due to elevated salinity and gas contents in deep aquifers. Progressive clogging of wells, pumps, pipes, valves and heat exchangers can cause major problems in geothermal heat and electric power production. In this context scale deposits constitute an environmental archive capturing installation-specific fluid-solid interaction over time, i.e. natural vs. man-made variations in fluid chemistry, temperature, pressure, outgassing (e.g. CO₂), flow rate and microbial activity. These factors control distinct crystal growth, variable porosity/density and lamination, accessory mineral and organic contents, chemical and isotopic compositions of the scales – and therefore the rates of inner-diameter reduction (scaling progress) and mechanical/chemical resistivity. In an approach of process understanding intuitively termed “Scaling Forensics” we apply state-of-the-art mineralogical and geochemical techniques combined with hydrogeochemical modeling and facility-specific data to reconstruct individual – favorable vs. unfavorable – environmental and technical conditions of scale formation. We collected carbonate scales and thermal waters from geothermal facilities distributed over the Hungarian Pannonian Basin covering a broad range of geogenic and man-made production conditions.

First results support distinct nucleation and crystal growth mechanisms influencing carbonate scale appearance and consistency. Crystallization on surfaces (substrates) typically results in more compact and resistant fabrics, whereas spontaneous particulate crystallization within an aqueous solution (in suspension) promotes increased porosity and therefore scaling progress. Steel corrosion layers can provide a highly attractive substrate for nucleation and ongoing crystal growth due to high specific surface areas and abundant defect sites of typical corrosion products. Moreover, corrosion layers of reduced mechanical resistivity (low crystallinity, hardness) may lead to preferred shearing-off along these layers. A prominent example of interplay between steel corrosion and carbonate scaling progress is discussed regarding the formation of cemented scale fragments (shards) damaging and blocking heat exchangers. We also conducted a first series of laboratory experiments to investigate some of the findings.

Purely inorganic can further be distinguished from microbially influenced carbonate precipitation. Microbial tissues might interact with basal corrosion layers and could be the explanation for prominent feather-like calcite crystals. The filamentous to dendritic structures probably foster the entrapment and accumulation of particles from suspension or provide nucleation sites for crystal growth. Next to an applied research focus we also discuss benefits from carbonate scales for fundamental geochemical method improvement. This involves the evaluation and calibration of novel and established isotope geothermometers using scales of diverse but well characterized precipitation conditions.

1. INTRODUCTION

The production of high salinity and gas-rich thermal water for heat- and electric power generation in geothermal doublet systems is frequently accompanied by diverse mineral precipitates (scaling) in wells, downhole pumps, transport pipes, valves and heat exchangers leading to a problematic reduction of inner diameters, disturbed flow regimes or complete clogging. Temperature and pressure changes occurring in different sections of geothermal installations promote extensive CO₂-degassing and/or steam separation and concomitant deposition of various carbonates, silica/silicates, sulfates, sulfides, oxyhydroxides or chlorides (e.g. Corsi, 1986; Regenspurg et al., 2015).

The particular mineralogy and scale characteristics depend on geogenic as well as man-made conditions, i.e. (hydro)geology, well depth, reservoir temperature and pressure, hydrochemistry, flow rate, operating pressure, geometry and transport materials of the geothermal facilities (cf. Finster et al., 2015). In low- to moderate enthalpy systems carbonate scaling is widespread due to elevated dissolved carbonate contents and carbon dioxide outgassing, e.g. resulting from (post)volcanic CO₂ contributions or CO₂ from degradation of organic matter in deep aquifers. Carbonate scales are most commonly met in the course of geothermal energy exploitation in Central Europe, e.g. from Devonian, Triassic, Upper-Jurassic and Tertiary (Neogene) limestone and dolomite aquifers of Hungary, Germany and Austria (Goldbrunner, 2000; Szanyi and Kovács, 2010; Stober, 2014). This is in contrast to the high enthalpy geothermal regions (Iceland, Tuscany, Mexico and others) where silica/silicate scaling typically dominates and carbonate precipitates occur only locally (Valdez et al., 2009; Zarrouk and Moon, 2014). In all regions, however, geothermal scaling is often interrelated to corrosion effects disintegrating carbon- and stainless steels, as well as concrete casings (Valdez et al., 2009; Mundhenk et al., 2013).

Our approach with regard to geothermal scales is based on mineralogical and hydrogeochemical analyses of these chemical sediments constituting an archive of fluid-solid interaction over time captured in their chemical composition and individual petrography, i.e. an approach henceforward termed “Scaling Forensics”. In other words, we attempt to reconstruct the temporally and spatially variable environmental and technical conditions determining favorable vs. unfavorable conditions for scaling, i.e. installation-specific short- vs. long-term nucleation and growth dynamics. This includes a detailed evaluation of fluid chemistry, pH- and redox conditions, temperature and pressure ranges, gas contents (CO₂, H₂S) and flow rate in view of process understanding and retarding measures of the scaling progress. In this context we apply state-of-the-art and mostly high-resolution geochemical methods based on our experiences in paleoenvironmental studies, i.e. speleothems and travertines as chemical archives (e.g.

Boch et al., 2011). Our forensic approach complements an increasing number of numerical modeling studies (Alt-Epping et al., 2013; Bozau et al., 2015) and both laboratory- and field-based experimental work (Hasson et al., 1996; Stáhl et al., 2000) investigating scaling and corrosion during geothermal energy production. It also relies on existing knowledge and experiences regarding geothermal reservoirs and scaling in the Hungarian Pannonian Basin (Bélteky, 1975; Ottlik, 1988; Pátzay et al., 2003; Horváth et al., 2015).

2. LOCATIONS, THERMAL WATERS & ANALYTICAL TECHNIQUES

Sampling locations of scales and thermal water include geothermal facilities for balneological, greenhouse heating and electric power generation purposes distributed over the Hungarian Pannonian Basin (Fig. 1). All of the selected sites suffer from carbonate scaling. The aquifer host rocks are mostly Triassic limestone/dolomite or Late-Miocene clastics. Sampling site selection was mainly based on significant scale formation, access to the geothermal facilities including basic technical and thermal water information. The production wells sampled represent a relatively wide range of depths (1000-2500 m), fluid-temperatures (40-100 °C), flow-rates (30-80 m³/h), operating pressures and water chemical compositions. Both carbonate scales and thermal waters were typically recovered from pipes at or close to the wellhead, i.e. before major CO₂-degassing (e.g. in gas separators).

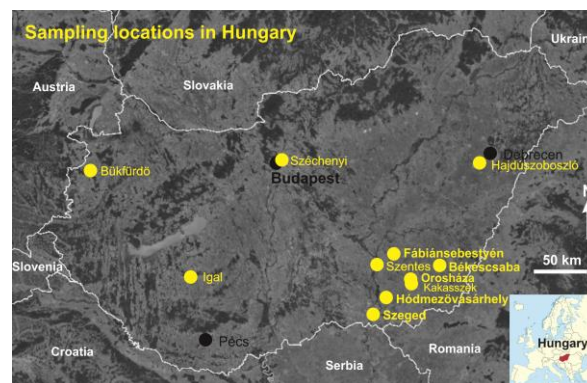


Figure 1: Locations of carbonate scale and thermal water sampling from geothermal facilities distributed over the Hungarian Pannonian Basin.

Thermal water sampling and in-situ measurements of hydrochemical parameters (T, EC, pH, alkalinity) from hot, mineral- and gas-rich water were challenging for operators and instruments. Major and minor ions, as well as trace elements in solution were analyzed in the laboratory (ion chromatography, ICP-OES, titrator) immediately after sampling. Distinct water types (Na-HCO₃, Na-HCO₃-Cl, Ca-Na-HCO₃-Cl-SO₄) depend on the region and aquifer characteristics. Total dissolved solids (TDS) contents measured so far range from 1298 to 15337 mg/l, pH

values from 6.2 to 7.7 and the waters often show high aqueous $p\text{CO}_2$ and overall gas contents. Hydrochemical equilibrium calculations reveal pronounced supersaturation with respect to CaCO_3 (calcite and to a minor degree aragonite) and thus support the carbonate scaling potential of most of these thermal waters. Stable water isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) measured (via cavity-ring-down-spectroscopy and isotope-ratio mass-spectrometry) from the waters allow of distinguishing cool climate (lighter) vs. warmer climate (heavier) groundwater of meteoric origin (close to Global Meteoric Waterline). These waters can be differentiated from mixtures with old (Tertiary) highly saline formation waters and fluids influenced by O-isotopic exchange with the host rocks. Dissolved inorganic carbon isotopes ($^{13}\text{C}_{\text{DIC}}$) help deciphering different sources of CO_2 and reflect site-specific conditions of groundwater evolution.

Regarding our forensic approach a detailed carbonate material characterization is crucial and is based on applying high-resolution (mm/ μm -range) cutting-edge analytical techniques. This includes computer-controlled micromill-sampling for stable carbon- and oxygen isotopic compositions of the carbonates, as well as laser-ablation (MC)-ICP-MS and electron microprobe analysis for minor/trace elemental compositions. Moreover, microscopic methods (optical, SEM) and hydrogeochemical modeling (PHREEQC software, Parkhurst and Appelo, 1999) combined with installation-specific data are envisaged. First results are promising with regard to evaluating favoring vs. retarding parameters determining the nucleation and progress of carbonate scaling.

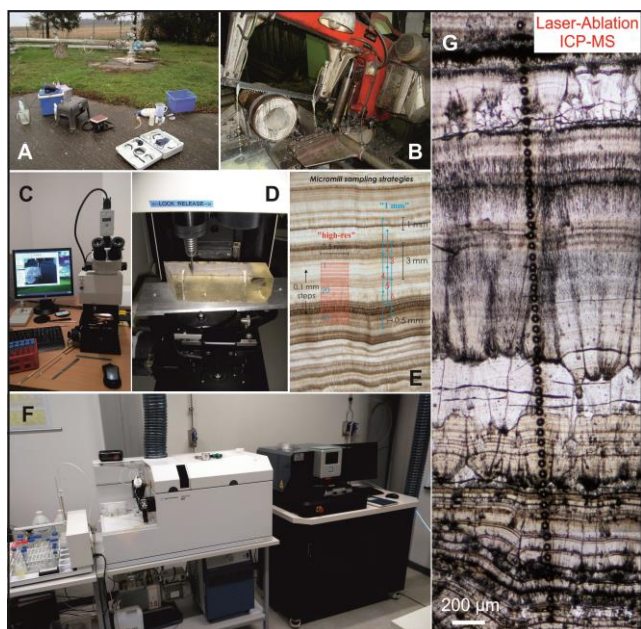


Figure 2: Selection of analytical approaches for studying geothermal scaling: A) Field-based hydrochemical and B) solid-phase (scale) sampling. C & D) Computer-controlled micromill sampling for high-resolution carbonate stable isotope profiles, E) applying different sampling strategies.

F & G) Laser-Ablation coupled (ICP) mass-spectrometry for high-resolution minor- and trace elemental profiles across scale growth layers.

3. CARBONATE SCALE GROWTH DYNAMICS

Mineral precipitates recovered from Hungarian Pannonian Basin geothermal installations show individual macroscopic characteristics including variable coloring, distinct crystal fabrics and porosity, (trace)elemental and detrital/organic contributions, as well as prominent lamination patterns (Fig. 3). The carbonate scaling samples of up to 10 cm thickness in pipes of different materials and mostly recovered near the wellheads represent mineral deposition from two weeks up to 45 years. As mentioned above, the scales archive installation-specific information on fluid-solid interaction, i.e. temporal changes in hydrochemistry, temperature and pressure, degassing rate (CO_2), flow rate and microbial activity manifested in distinct crystal nucleation and growth, variable porosity/density and lamination, chemical and isotopic compositions. Importantly, these factors directly translate into the scaling progress, i.e. the rate of inner-diameter reduction and mechanical/chemical resistivity of the unwanted scales. In this context, different pipe materials (various steels and plastics, specific coatings) play a significant role regarding the initiation and evolution of the scales. The narrow laminations or longer-term petrographic zonations observed in many scales (Fig. 3) often represent rhythmic growth successions, for example seasonal rhythms reflecting winter vs. summer operation, effects from periodical maintenance or event-like corrosion layers after major production cessations. Irregular scale growth morphologies (cf. Fig. 3, down right) often result from a two-phase fluid flow within the pipes, i.e. a high gas-water ratio directing the liquid phase and active carbonate precipitation towards the bottom and sides in a horizontal pipe when the lower density gaseous phase streams within the upper section.

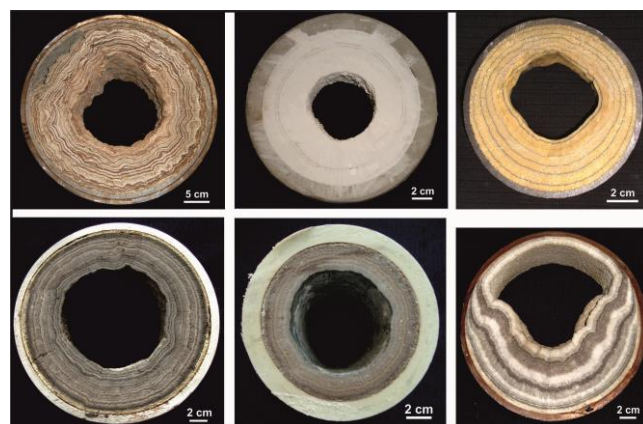


Figure 3: Multi-annual carbonate scales from Pannonian Basin geothermal facilities displaying an individual macroscopic appearance (coloring, morphology, porosity, lamination) depending on geogenic and man-made environmental conditions.

Powder X-ray diffraction (XRD) and Fourier-transform infrared-spectroscopic (FT-IR) analyses show that all of the collected scales consist nearly entirely of anhydrous calcium carbonate, i.e. low or high Mg-calcite and occasionally aragonite. Whitish colored scales (Fig. 3) consist of pure CaCO_3 (or sulfates forming in some boreholes; not included in this study). Particular colors of the carbonate scales further depend on the nature and concentration of minor contaminations. Red-brownish layers (Fig. 3, upper-left) are mostly stained with iron-(oxy)hydroxides (e.g. FeOOH), partly from steel corrosion in the geothermal systems. Grey to black colored scales (Fig. 3, bottom images and Fig. 4) result from contributions of sulphides (FeS , CuFeS_2 , Fe-rich ZnS , CuS , NiS), siliciclastic contents (muscovite, quartz, feldspar, clinochlore) and/or variable hydrocarbon contents (aliphatic and aromatic compounds). Metal ions might come from a geogenic source (e.g. organic-rich shales) or from mobilization of metals during steel corrosion (e.g. by H_2S). Siliciclastic, detrital contaminants probably originate from mobilization of fine-grained sediment in the aquifer or from borehole sidewalls. A contribution of different hydrocarbons in some dark scales is supported by relatively high organic carbon (TOC) contents measured in some of the thermal waters (45–115 mg/l) and by a broad spectrum of organic carbon species reported from Pannonian Basin formation waters often associated with oil reservoirs (Varsányi et al., 2002).

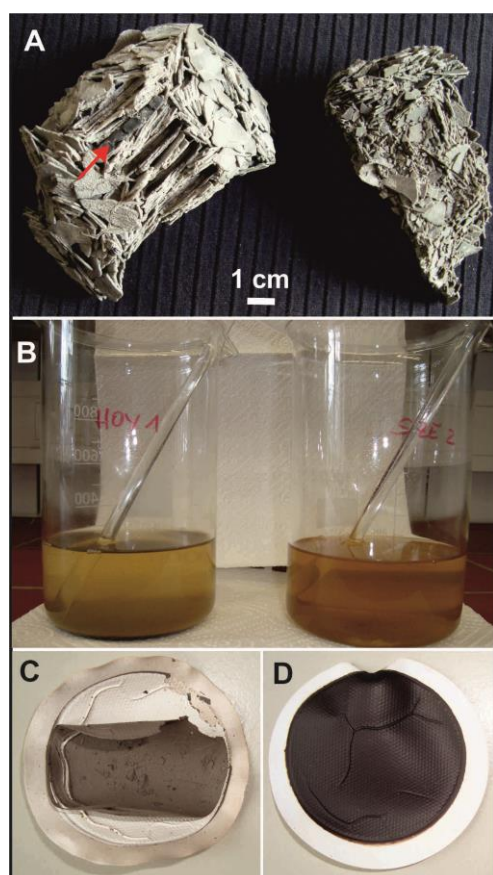


Figure 4: A) Dark Mg-calcite scale consisting of multiple cemented fragments blocking a heat

exchanger. Red arrow denotes a remaining rubber gasket. B) Digestion of dark scales from two different locations in nitric acid in order to extract the chromophoric contamination. C & D) Two different types of black residuum on acetate filters (5 cm).

3.1 Nucleation & Crystal Growth Mechanisms

Specific crystallization mechanisms play a crucial role with regard to the initiation and progress of scale precipitation, i.e. crystal growth principles determine the appearance and characteristics of scales significantly. Inorganic precipitation can be distinguished from microbially influenced crystallization. Microbes (bacteria, algae, fungi) can actively influence carbonate nucleation or may serve as a more passive nucleation substrate comparable to microbial activity in travertine forming streams (e.g. Fouke, 2011). Regarding inorganic carbonate precipitation two major crystal growth mechanisms are represented by wall crystallization (on surfaces) versus suspended particulate crystallization (in solution; cf. Bramson et al., 1995). Importantly, the fundamentally different mechanisms might result in compact vs. more porous growth layers in the scales (Fig. 5). Wall crystallization is characterized by nucleation and ongoing crystal growth requiring a substrate, e.g. pipe surfaces of various materials. Microscopically, such scale growth layers typically show nearly parallel, columnar, competitively growing, i.e. prominently oriented crystals indicating continuous and regular crystal growth by ion supply from the aqueous solution (Fig. 5C, D, E). Typical features further include low inter- and intracrystalline porosity, well developed (rhombohedral) crystal tips (Fig. 5B) and laminated sequences where lamina thicknesses reflect the average crystal sizes (Fig. 5C, E). All of these crystal growth characteristics promote a rather compact/dense carbonate scale fabric. In contrast, suspended particulate scale deposition is characterized by spontaneous nucleation of small (micritic) carbonate crystals within the thermal water flow and subsequent agglomeration, compaction and cementation (partial recrystallization) on the active scale growth surface. This mechanism results in a more random orientation of the individual crystals and most importantly in a porous scale fabric promoting a rapid scaling progress, i.e. increased reduction of inner diameters in boreholes and transport pipes (Fig. 5A, B). Next to the dominant crystal growth mechanism the proportion of pores in the scale and therefore its density and also resistivity depend on the precipitation rates, i.e. faster crystallization resulting in an overall increased porosity. The occurrence of a particular crystal growth mechanism strongly depends on the degree of carbonate supersaturation of the thermal fluid and consequently on natural as well as anthropogenically controlled conditions. Spherical and needle-shaped aragonite crystals observed in a thick carbonate scale from Budapest (Fig. 3, upper-left) are primarily dispersed within porous micritic calcite

layers. This suggests an origin of the aragonite from spontaneous particulate nucleation and subsequent agglomeration and cementation in the scale at occasionally prevailing higher carbonate supersaturation associated with unfavorable thermal water production conditions, e.g. increased outgassing, reduced flow or temperature fluctuations.

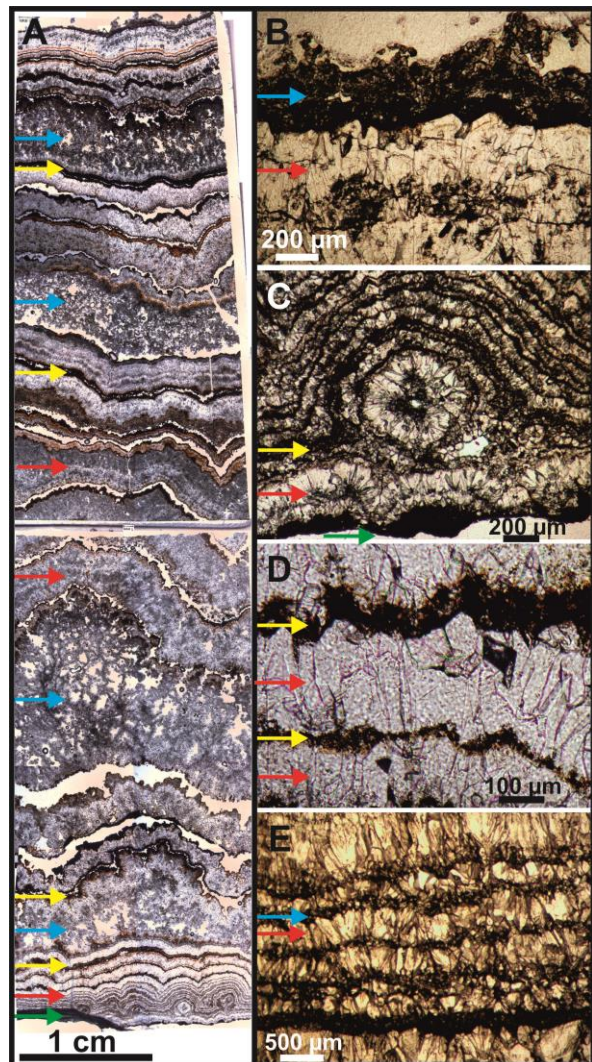


Figure 5: Microscopic (transmitted-light) images showing A) thick scale consisting of distinct layers of highly variable thickness. More compact wall crystallization (red arrows) is distinguished from more porous spontaneous/suspended particulate nucleation/agglomeration (blue arrows); Iron-mineral-rich layers (from corrosion) are common within many scales (yellow arrows) and at basal (pipe) contacts (green arrows). B) Youngest section (top) of a scale showing wall- vs. particulate scaling progress separated by idiomorphic rhombohedral calcite crystal tips. C) Basal section displaying abundant crystallite nucleation on corrosion layers, prevailing wall crystallization and disturbed lamination due to a spherical component. D) Red-brownish layers of variable thickness made of iron-mineral particles most likely resulting from steel corrosion and separating compact calcite layers. E) Another carbonate scale supporting distinct crystal growth mechanisms and associated characteristics.

3.2 Corrosion vs. Scaling

Corrosion processes are widespread in geothermal installations due to the characteristic deep thermal water (saline) chemical compositions and pipe materials used. Scale nucleation often starts on a corroded inner surface of a borehole liner or transport pipe and fragments of these corrosion layers are frequently present at the base of scale samples (Fig. 5A, C). Alternatively, indicative red-brownish layers probably deriving from steel corrosion repeatedly occur within the scales, i.e. they are an expression of the variable thermal water production dynamics of a geothermal facility and are often prominently manifested in lamination patterns (Fig. 5). The red-brownish stain is indicative of iron-mineral-rich compositions and in particular of iron-(oxy)hydroxides such as $\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$ (ferrihydrite) or FeOOH (goethite). These initial iron phases hold a low degree of crystallinity and high specific surface areas and are recrystallized towards more crystalline Fe_3O_4 (magnetite) or Fe_2O_3 (hematite) with time. Corrosive layers, however, in some cases (or sections) also include the occurrence of iron-sulphides resulting from chemical reactions of steel with H_2S . In principle, the dominant corrosion phases strongly rely on the prevailing redox conditions, i.e. mostly on the oxygen concentrations in aqueous solution. Under the microscope the red-brownish intervals within the carbonate scales consist of tiny colored particles arranged in clusters and layers of laterally variable thickness frequently tracing rhombohedral crystal tips (Fig. 5D). These characteristics support an origin from abrasion and flushing as suspended particles following steel corrosion and subsequent adsorption and agglomeration on the scale growth surface. Such iron-particle delivering events might be enhanced after extended time intervals of stagnant water in transport pipes, heat exchangers and radiators, e.g. summertime cessation of thermal water production and cold season restart and flushing. A minor contribution of iron phases in the scales could also derive from iron- and metal-rich aquifers via precipitation from aqueous solution or mobilization in suspension.

In the context of corrosion versus scaling the carbonate precipitates can offer some protective effects with regard to progressive corrosion (cf. Mundhenk et al., 2013). Some physicochemical reactions support both, scale deposition and formation of corrosion minerals, e.g. increasing pH values in the course of pronounced CO_2 -degassing foster carbonate precipitation, as well as FeOOH formation (cf. Alt-Epping et al., 2013). Based on our observations, however, the corrosion layers at the scale-substrate-interface and also within the scale successions constitute an attractive substrate for carbonate nucleation and ongoing crystal growth expressed in the abundant (micro)crystallites populating the initial scale coatings (Fig. 5C & Fig. 6A, B). This can be explained by the low degree of crystallinity, abundant defect sites and high specific surface areas of typical steel corrosion minerals (e.g. “hydrous ferric oxides”).

Furthermore, corrosion layers of low crystallinity and hardness implicate a reduced mechanical resistivity leading to preferred shearing-off along these layers both at the scale bases (pipe-contact) and within the carbonate scales (Fig. 6A).

A prominent example of a key interplay between steel corrosion and carbonate scaling progress might be the formation of cemented scale shards damaging and blocking heat exchangers (cf. Fig. 4A). Apart from the natural conditions supporting scale formation the respective chain of unfavorable circumstances could start with major corrosion of steel pipes resulting in an attractive substrate for initial carbonate nucleation and further crystal growth. A wall crystallization mechanism promotes idiomorphic (Mg-calcite) crystals showing prominent rhombohedral crystal tips and consequently featuring a rough scale surface. The latter supports a relatively high flow resistance and probably a more turbulent flow regime at the scale surface. High overall flow rates and increased turbulence in combination with the reduced mechanical resistivity of the basal corrosion layer (pipe contact) and the rough scale surface can result in a local exfoliation of scale shards. Over time more of the scale shards are advected towards the heat exchangers potentially leading to impact damages and ongoing agglomeration, cementation and severe clogging. This example highlights the need for a more detailed process understanding of corrosion characteristics in relation to scaling growth dynamics.

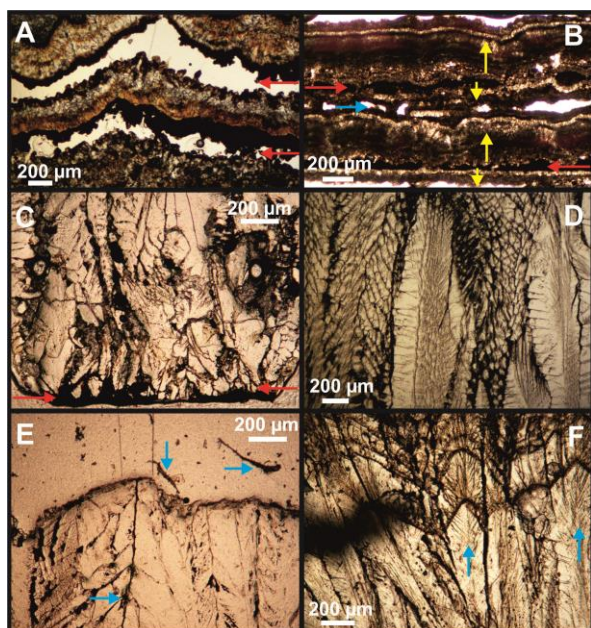


Figure 6: Microscopic (TL) insights of A) preferred internal disintegration of scales along particulate corrosion layers (arrows). B) Two cemented scale fragments (shards) recovered from a heat exchanger (cf. Fig. 4A) showing abundant bidirectional (yellow arrows) nucleation on corrosion layers (red arrows) and later stage cementation by carbonate (blue arrow). C) Evidence of filamentous to dendritic microbial tissues populating a basal scale corrosion layer. D)

Typical feather-like dendritic or flaked calcite crystals probably formed in association with active or passive microbial activity. E) Sparse remnants of microbial filaments/dendrites (blue arrows) from a scale top featuring feather-like crystals. F) Another scale supporting the relation of microbial substrates and the relatively large feather crystals.

3.3 Microbial Activity vs. Scaling

In several of the carbonate scale samples studied we find some evidence for microbial activity being present and probably influencing scale deposition and corrosion in some ways. An increasing number of investigations (e.g. Lerm et al., 2013; Würdemann et al., 2014) highlight the potential role of (hyper)thermophilic and halophilic, anaerobic and aerobic (e.g. sulfate-reducing/sulfur-oxidizing) microbial communities (mainly bacteria, ev. algae and fungi) with regard to corrosion and mineral precipitation in geothermal installations. These microorganisms populate (organic/sulfur-rich) aquifers, wells, transport pipes and storage tanks and their specialized metabolism utilizes various substrate materials (plastics, carbon/stainless steels) and/or thermal water contents resulting in bio-catalytically enhanced corrosion (e.g. pitting).

Sparse remnants or traces of filamentous structures or dendritic networks indicative of former microbial activity are observed at some carbonate scale vs. substrate interfaces (scale-base), as well as within some sections of the scale deposits (Fig. 6). In general, however, the organic structures suffer from poor preservation, i.e. they are decomposed rapidly. Regarding the initial microbial populations on steel pipes (Fig. 6C), bacterially induced oxidation of iron and progressive corrosion might play a significant role. As mentioned above, the corrosion layers then provide an attractive substrate for carbonate crystal nucleation and ongoing scale formation (Fig. 5C, D). The braided biofilms might also have some function with respect to active or passive carbonate scale formation comparable to microbial communities of hot springs and streams influencing travertine and calcareous tufa formation (Chafetz and Guidry, 1999; Fouke, 2011). More specific, the dendritic structures and filaments observed could foster the entrapment and accumulation of particles from suspension or provide nucleation sites for initial carbonate crystal growth. In both cases small crystallites might further evolve ((re)crystallize) towards larger, competitive, columnar crystals. A prominent feature in some of our scales is feather-like calcite crystals resembling dendritic to flaked fabrics (Fig. 6D-F). The formation of such crystal morphologies might be closely associated with microbial filaments (center of the relatively large crystals) and dendrites (crystal branches). We anticipate further scaling petrographic studies in order to better constrain this aspect in our samples. Considering the diverse and prominent lamination patterns in the carbonate scales, microbial

(re)colonization might also be important in some of the scales, e.g. the establishment or decay of biofilms during production or maintenance intervals. Microbial coatings on active scale growth surfaces could also entail a relatively rough inner surface affecting the thermal fluid flow (flow resistance, turbulences) eventually facilitating local dismantling/mobilization of scale fragments or increased outgassing in a more turbulent flow regime. In essence, microbial activities have to be considered in various aspects of scaling as well as corrosion and carbonate scales constitute an environmental archive regarding a forensic reconstruction of such biological contributions.

4. CRYSTALLIZATION EXPERIMENTS

Another approach of studying scale formation in geothermal settings and in particular the dominant nucleation and crystal growth mechanisms is achieved with laboratory experiments. In a first series we have investigated different widespread scale substrates interacting with synthetic thermal water in glass batch reactors that were placed into climate cabinets at constant reaction temperatures of 30, 60 and 90 °C for seven weeks (Fig. 7). The artificial substrates (disks) involved materials frequently used in geothermal applications, i.e. stainless steel, galvanized steel, rubber seal (comparable to those in heat exchangers) that were placed (hanging freely) into the glass batch reactors (Fig. 7A, B C). Synthetic thermal water of relatively high ionic strength (salinity) and consequently scaling potential was prepared from two parent aqueous solutions containing 1) NaHCO_3 , NaCl and 2) $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, NaCl , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$. These two multi-component parent solutions were mixed in the glass batch reactors in order to trigger carbonate precipitation. More specific, this setup allows to separate wall crystallization (on artificial substrate and reactor glass wall) from spontaneous, particulate nucleation (direct sedimentation from water column). In addition, we examine the temperature- and crystallization-dependent incorporation of Mg, Sr and Ba into CaCO_3 . Initial vs. final (after seven weeks) aqueous solutions, as well as the mineral precipitates were sampled and studied by various analytical techniques.

Preliminary results showed the occurrence of the different CaCO_3 polymorphs calcite, aragonite and vaterite depending on the respective physicochemical conditions, i.e. mainly temperature and substrate. As a minor constituent a zinc-carbonate phase – $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ (hydrozincite) – was detected in the galvanized-steel experiments. In general, enhanced carbonate precipitation (scale deposition) was observed at elevated temperature reflected in the amount of solids and the final hydrochemistry. In most experiments a major proportion of precipitates settled from suspension (spontaneous nucleation) and this suspended particulate crystallization mechanism is more important at higher temperatures (60 and 90 °C). The results obviously support a significant influence of the provided substrate. Distinct crystal shapes dominate at different temperatures and substrate

materials. For example, highest intra-crystalline porosity of calcite crystals is manifested at 90 °C, probably induced by increased precipitation rates. Compared to data inferred from carbonate scale samples collected in-situ from geothermal facilities the experiments provide valuable additional evidence. Aragonite constitutes a prominent phase at higher temperatures (90 °C) and is primarily originating from particulate nucleation in suspension (Fig. 7E) also suggested by detailed scale investigations (cf. chapter 3.1). Experiments applying galvanized steel disks showed strong corrosion – in particular at 90 °C reaction temperature (Fig. 7B). Abundant rhombohedral crystals of calcite and some spherical hydrozincite densely covered the substrate (Fig. 7D). Removal of subsamples demonstrated a strong adherence of the carbonate scale onto the corroded substrate and further a red-brownish stain of the carbonate precipitates locally. Moreover, partial exfoliation of the corrosion layers is observed (cf. chapter 3.2).

Considering further laboratory experimental work the testing of additional scale substrate materials commonly or potentially used in geothermal applications is anticipated. A focus will be given on studying the effect of different degrees of corrosion on scale nucleation and progression.

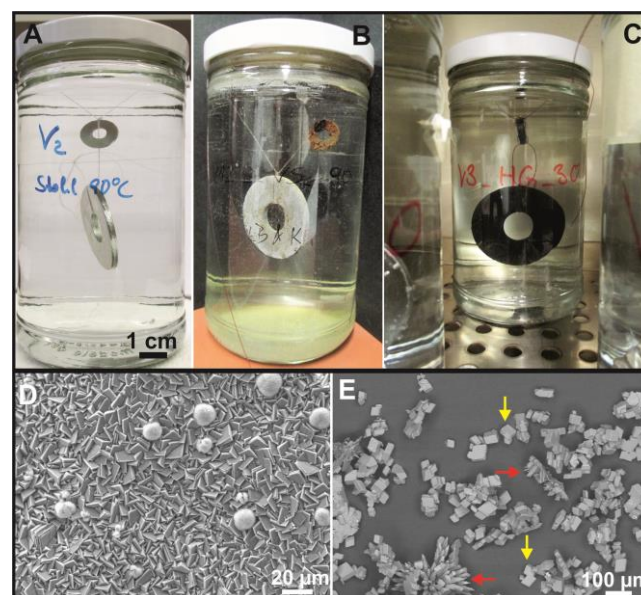


Figure 7: Laboratory experiments of carbonate scale crystallization on artificial substrates. A) Galvanized steel disks of different sizes submerged in synthetic thermal water of 90 °C in the beginning and B) end of the chemical reaction period. Note the heavy corrosion and whitish carbonate precipitates after seven weeks. C) Glass reactor containing rubber seals placed in a climate cabinet of constant temperature. D) Dense cover of rhombohedral calcite and sparse hydrozincite on galvanized steel substrate. E) Calcite crystals (yellow arrows) and acicular, spherical aragonite (red arrows) co-precipitated by spontaneous, particulate nucleation (settled from suspension).

5. NOVEL & TRADITIONAL STABLE ISOTOPE THERMOMETERS

Next to an applied and problem-solving research focus, we also anticipate benefits from studying carbonate scales in detail with regard to fundamental geochemical method improvement. This primarily includes the evaluation and calibration of novel (multiply-substituted or “clumped”; Eiler, 2007; Kluge et al., 2015) and established (e.g. $^{18}\text{O}/^{16}\text{O}$) stable isotope geothermometers. In this context carbonate scales of well characterized formation conditions are of particular value. Also, scale precipitates of geothermal settings provide a broad range of hydrochemical compositions, temperatures, pH values and ionic strengths affecting isotope fractionation, e.g. kinetic vs. equilibrium fractionation effects.

The development of multiply-substituted isotope geothermometers recently gains in importance for paleoenvironmental research (e.g. based on corals, lake carbonates, speleothems), as well as regarding diagenesis studies and upcoming applications in the hydrocarbon industry. These geothermometers hold the advantage of inferring mineral formation temperatures from solid-phase isotopic compositions (e.g. of various carbonates) directly, i.e. without the need of knowing the corresponding (past) fluid isotopic composition (Eiler, 2007). First clumped isotope measurements conducted on some of our carbonate scales reproduce the actual site-specific formation (water) temperatures surprisingly well. Selected scales will be studied for specific effects (e.g. pH and aqueous speciation effects) on ^{13}C - ^{18}O clumping in carbonates.

With regard to traditional stable carbon and oxygen isotope analyses the Pannonian Basin carbonate scales reveal a broad $\delta^{18}\text{O}$ range mainly reflecting the site-specific differences in water-temperatures, the origin and age (aquifer depth) of the thermal waters (Fig. 8). The C isotope values of the solid carbonate scales, in contrast, reveal a narrow range ($\delta^{13}\text{C}$ from -3 to +3 ‰ VPDB) reflecting the regional CO_2 and dissolved inorganic carbon sources. Individual scale samples typically show relatively constant values (characteristic of the borehole) and only few samples display major variations (e.g. SZI; Fig. 8).

Measurements of oxygen isotope fractionation between thermal water and precipitating scale carbonate from different geothermal facilities and temperature regimes reveal a strong temperature dependence and (near)-equilibrium isotopic fractionation conditions. The latter is based on applying empirical (field-based) O-isotope fractionation constraints partially extrapolated to higher temperatures (Coplen, 2007; Demény et al., 2010). Considering the potential significance of specific effects, however, we anticipate a detailed study on $\delta^{18}\text{O}$ vs. temperature relationships based on selected carbonate scales solely.

In the light of the strong and obviously systematic temperature dependence of the scale O-isotopic compositions an interesting scaling forensic application consists in a temporally highly-resolved reconstruction of water-temperature changes using micromilled oxygen isotope profiles across the scale deposits. Next to a temperature control, however, longer-term changes in thermal water $\delta^{18}\text{O}$ from aquifer dynamics (e.g. variable borehole influges) have to be considered. Tackling the above-mentioned potential we started analyzing a 7.5 cm thick (deposited from 1967 to 2012) carbonate scale deposited in a major transport pipe leaving a thermal water storage tank towards a spa resort at high spatiotemporal resolution.

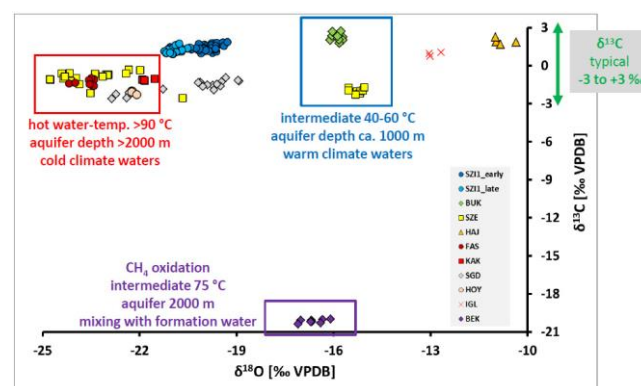


Figure 8: Scale carbonate C and O isotope compositions primarily reflecting the site-specific and highly different water-temperatures, origin and age (aquifer depth) of the thermal waters, as well as the sources of dissolved CO_2 .

6. CONCLUSION & OUTLOOK

Our analytical approach and first results demonstrate:

- Carbonate scales constitute a valuable environmental archive capturing natural and man-made variations of fluid-solid interaction (site-specific production dynamics) over time in their characteristic chemical and petrographic compositions. Detailed analysis applying state-of-the-art mineralogical and geochemical techniques opens the door for a better understanding of scale nucleation and progress considering favorable vs. unfavorable precipitation conditions (“Scaling Forensics”).
- A diverse set of carbonate scales from the Hungarian Pannonian Basin reveals specific nucleation and crystal growth mechanisms playing a crucial role for major scale properties, e.g. porosity and mechanical resistivity. Inorganic precipitation is distinguished from microbially influenced crystallization. Two major crystal growth mechanisms consist in “wall crystallization” versus “suspended particulate crystallization”.
- Steel corrosion and scaling progress are intimately related. Corrosion layers can provide an attractive substrate for carbonate nucleation and ongoing crystal

growth or result in a reduced mechanical resistivity leading to preferred shearing-off along such layers. The common occurrence of scale fragments (shards) damaging and clogging heat exchangers might strongly rely on these interplays.

- We also find some evidence of microbial activity potentially influencing the scaling progress and eventually steel corrosion in some installations. Microbial structures are encountered at the scale vs. substrate (pipe) interface, as well as within some sections of the scales.

- Laboratory experiments yield valuable additional insights regarding the dominant nucleation/crystal growth mechanisms on different substrates. Batch reactor experiments showed different CaCO₃ polymorphs, variable crystal shapes, porosity and crystallization mechanisms (wall- vs. particulate) depending on the prevailing environmental conditions (temperature, substrate).

- The unwanted carbonate scales forming within a broad range of water compositions, temperatures, pH values and ionic strengths provide some major benefits for fundamental geochemical method improvement, i.e. the evaluation and calibration of novel “clumped” and established stable isotope geothermometers. Scales of well characterized formation conditions are of particular value.

A fertile playground for future studies comprises of:

- An increased process understanding of scale growth dynamics in relation to corrosion effects.

- Measurement of high-resolution laser-ablation ICP-MS profiles of strontium and barium concentrations in the carbonate scales. The latter ion incorporation into CaCO₃ is known to strongly depend on precipitation rate (e.g. Tang et al., 2008) and is therefore a promising tool regarding scaling progress and distinguished nucleation/crystal growth mechanisms.

- Measurement of high-resolution stable isotope profiles in order to reconstruct water temperature fluctuations (O-isotopes), as well as variable CO₂-degassing and concomitant mineral precipitation (C-isotopes).

- Modeling potential effects of rough scale surfaces versus fluid flow (flow resistance, turbulences, increased outgassing) versus corrosion and local exfoliation of scale fragments damaging and clogging heat exchangers.

- Experimental work focusing on different degrees of corrosion affecting scale nucleation and progress.

- Understanding active vs. passive roles of microbial activity, i.e. inducing corrosion and/or crystallization, supporting agglomeration and providing an attractive substrate for scale deposition.

- Finally, we anticipate a fundamental study on oxygen- and clumped isotope fractionation vs. temperature, pH and ionic strengths based on selected carbonate scales exclusively.

REFERENCES

- Alt-Epping, P., Waber, H. N., Diamond, L. W. and Eichinger, L.: Reactive transport modeling of the geothermal system at Bad Blumau, Austria: Implications of the combined extraction of heat and CO₂, *Geothermics*, **45**, (2013), 18-30.
- Béteky, L.: Problems related to operating thermal wells subject to scaling in Hungary, *Geothermics*, **4**, (1975), 57-65.
- Boch, R., Spötl, C. and Frisia, S.: Origin and palaeoenvironmental significance of lamination in stalagmites from Katerloch Cave, Austria, *Sedimentology*, **58**, (2011), 508-531.
- Bozau, E., Häußler, St. and van Berk, W.: Hydrogeochemical modelling of corrosion effects and barite scaling in deep geothermal wells of the North German Basin using PHREEQC and PHAST, *Geothermics*, **53**, (2015), 540-547.
- Bramson, D., Hasson, D. and Semiat, R.: The roles of gas bubbling, wall crystallization and particulate deposition in CaSO₄ scale formation, *Desalination*, **100**, (1995), 105-113.
- Chafetz, H. S. and Guidry, S. A.: Bacterial shrubs, crystal shrubs, and ray-crystal shrubs: bacterial vs. abiotic precipitation, *Sedimentary Geology*, **126**, (1999), 57-74.
- Coplen, T. B.: Calibration of the calcite–water oxygen-isotope geothermometer at Devils Hole, Nevada, a natural laboratory, *Geochimica et Cosmochimica Acta*, **71**, (2007), 3948-3957.
- Corsi, R.: Scaling and corrosion in geothermal equipment: problems and preventive measures, *Geothermics*, **15**, (1986), 839-856.
- Demény, A., Kele, S and Siklósy, Z.: Empirical equations for the temperature dependence of calcite-water oxygen isotope fractionation from 10 to 70 °C, *Rapid Communication in Mass Spectrometry*, **24**, (2010), 3521-3526.
- Eiler, J. M.: “Clumped-isotope” geochemistry – The study of naturally-occurring, multiply-substituted isotopologues, *Earth and Planetary Science Letters*, **262**, (2007), 309-327.
- Finster, M., Clark, C., Schroeder, J. and Martino, L.: Geothermal produced fluids: Characteristics, treatment technologies, and management options, *Renewable and Sustainable Energy Reviews*, **50**, (2015), 952-966.
- Fouke, B. W.: Hot-spring Systems Geobiology: abiotic and biotic influences on travertine formation at Mammoth Hot Springs, Yellowstone

- National Park, USA, *Sedimentology*, **58**, (2011), 170-219.
- Goldbrunner, J. E.: Hydrogeology of Deep Groundwaters in Austria, *Mitt. Österr. Geol. Ges.*, **92**, (2000), 281-294.
- Hasson, D., Bramson, D., Limoni-Relis, B. and Semiat, R.: Influence of the flow system on the inhibitory action of CaCO₃ scale prevention additives, *Desalination*, **108**, (1996), 67-79.
- Horváth, F., Musitz, B., Balázs, A., Végh, A., Uhrin, A., Nádor, A., Koroknai, B., Pap, N., Tóth, T. and Wórum, G.: Evolution of the Pannonian basin and its geothermal resources, *Geothermics*, **53**, (2015), 328-352.
- Kluge, T., John, C. M., Jourdan, A.-L., Davis, S. and Crawshaw, J.: Laboratory calibration of the calcium carbonate clumped isotope thermometer in the 25–250 °C temperature range, *Geochimica et Cosmochimica Acta*, **157**, (2015), 213-227.
- Lerm, S., Westphal, A., Miethling-Graff, R., Alawi, M., Seibt, A., Wolfgramm, M. and Würdemann, H.: Thermal effects on microbial composition and microbiologically induced corrosion and mineral precipitation affecting operation of a geothermal plant in a deep saline aquifer, *Extremophiles*, **17**, (2013), 311-327.
- Mundhenk, N., Huttenloch, P., Sanjuan, B., Kohl, T., Steger, H. and Zorn, R.: Corrosion and scaling as interrelated phenomena in an operating geothermal power plant, *Corrosion Science*, **70**, (2013), 17-28.
- Ottlik, P.: Geothermal experience in Hungary, *Geothermics*, **17**, (1988), 531-535.
- Parkhurst, D. L. and Appelo, C. A. J.: User's guide to PHREEQC (Vers. 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, *U.S. Geological Survey Water-Resources Investigations Report*, **99-4259**, (1999), 312 pp.
- Pátzay, G., Kármán, F. H. and Póta, G.: Preliminary investigations of scaling and corrosion in high enthalpy geothermal wells in Hungary, *Geothermics*, **32**, (2003), 627-638.
- Regenspurg, S., Feldbusch, E., Byrne, J., Deon, F., Driba, D. L., Henniges, J., Kappler, A., Naumann, R., Reinsch, Th. and Schubert, Ch.: Mineral precipitation during production of geothermal fluid from a Permian Rotliegend reservoir, *Geothermics*, **54**, (2015), 122-135.
- Stáhl, G., Pátzay, G., Weiser, L. and Kálmán, E.: Study of calcite scaling and corrosion processes in geothermal systems, *Geothermics*, **29**, (2000), 105-119.
- Stober, I.: Hydrochemical properties of deep carbonate aquifers in the SW German Molasse basin, *Geothermal Energy*, **2**, 13, (2014), 1-20.
- Szanyi, J. and Kovács, B.: Utilization of geothermal systems in South-East Hungary, *Geothermics*, **39**, (2010), 357-364.
- Tang, J., Köhler, St. J. and Dietzel, M.: Sr²⁺/Ca²⁺ and ⁴⁴Ca/⁴⁰Ca fractionation during inorganic calcite formation: I. Sr incorporation, *Geochimica et Cosmochimica Acta*, **72**, (2008), 3718-3732.
- Valdez, B., Schorr, M., Quintero, M., Carrillo, M., Zlatev, R., Stoytcheva, M. and de Dios Ocampo, J.: Corrosion and scaling at Cerro Prieto geothermal field, *Anti-Corrosion Methods and Materials*, **56**, (2009), 28-34.
- Varsányi, I., Kovács, L. Ó., Kárpáti, Z. and Matray, J.-M.: Carbon forms in formation waters from the Pannonian Basin, Hungary, *Chemical Geology*, **189**, (2002), 165-182.
- Würdemann, H., Westphal, A., Lerm, St., Kleyböcker, A., Teitz, S., Kasina, M., Miethling-Graff, R., Seibt, A. and Wolfgramm, M.: Influence of microbial processes on the operational reliability in a geothermal heat store – Results of long-term monitoring at a full scale plant and first studies in a bypass system, *Energy Procedia*, **59**, (2014), 412-417.
- Zarrouk, S. J. and Moon, H.: Efficiency of geothermal power plants: A worldwide review, *Geothermics*, **51**, (2014), 142-153.

Acknowledgements

We thank Judith Jernej for ion chromatographic analysis of thermal waters, Maria Hierz for TOC analyses, Andre Baldermann and Andrea Wolf for conducting ICP-OES measurements and Sylvia Perchthold for carbonate stable isotope sampling. Peter Sipos is acknowledged for providing first μ -XRD estimates and Michael Wedenig for sharing experiences regarding hydrothermal experiments. Magdolna Virág's and Szabolcs Leél-Össy's efforts in collecting a scale-sample from Széchenyi Spa are also acknowledged. Chemical and mineralogical analyses were conducted at NAWI Graz Central Lab for Water, Minerals and Rocks.