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Department of Earth Sciences
Georesources Switzerland Group

Lithium in geothermal brines

Status report on the current situation in Switzerland and in neighbouring countries

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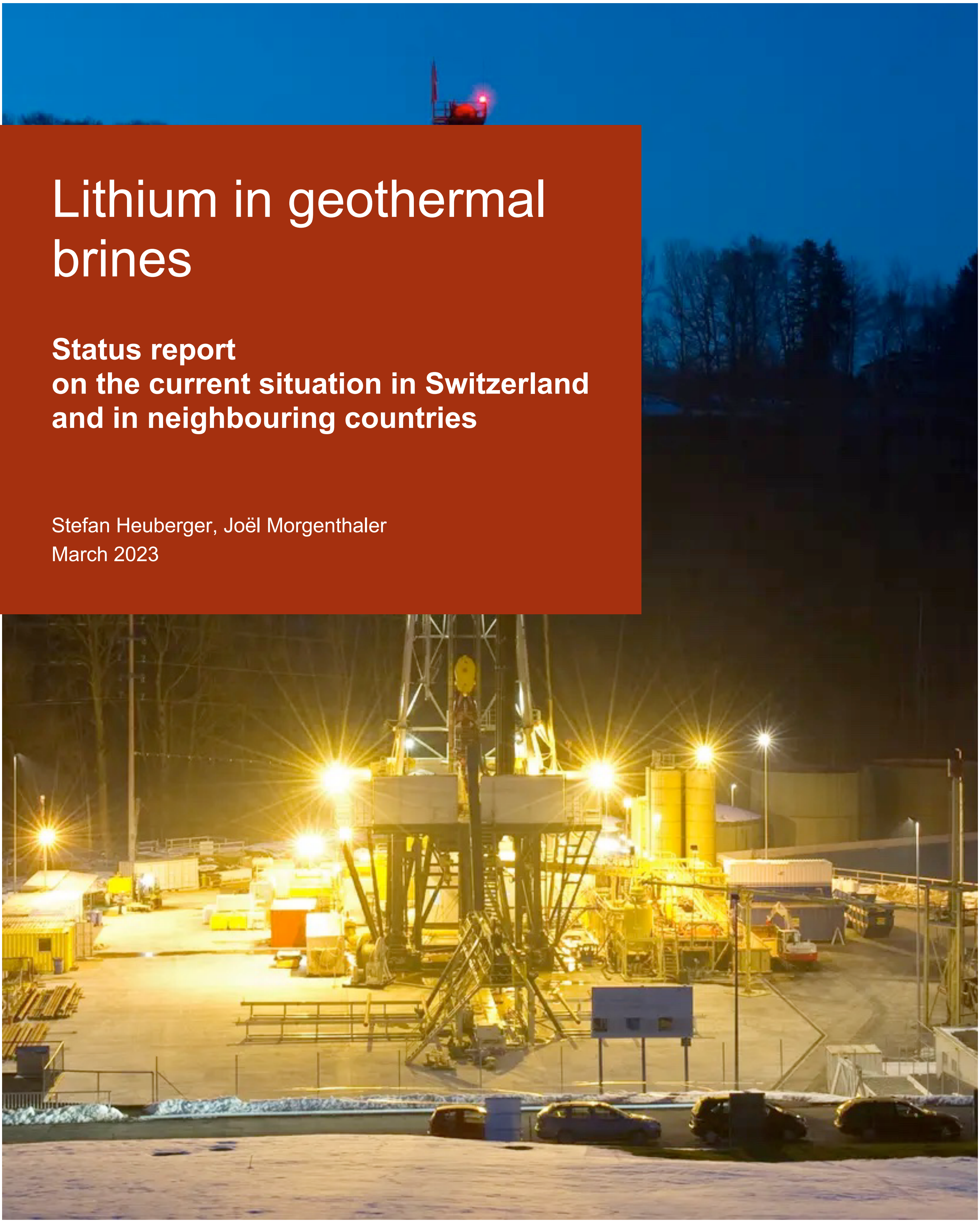

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Cover photo: Geothermal well St.Gallen GT-1, March 2013, St.Gallen (Switzerland).
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Contents

1 Foreword

Deep geothermal energy is one of the important energy sources envisioned in the Energy and Heat Strategies 2050 by the Swiss Federal Office of Energy (SFOE 2018, 2023). Deep drilling projects are associated with high costs. Therefore, such projects require a careful selection of the promising drilling sites and a robust business case. Depending on the geological setting, some geothermal fluids are known to contain economic amounts of critical raw materials (e.g. lithium, cobalt, nickel) that are of importance for the energy transition (European Commission 2022). These raw materials are needed for the manufacturing of batteries or other high-tech products. To expand their portfolio and optimise production costs, some energy companies aim to combine the production of geothermal energy with the extraction of lithium from the fluids recovered from the geothermal wells.

It remains to be assessed whether, and to what extent, the geothermal fluids in Switzerland contain relevant amounts of minerals or metals that could justify their economic recovery.

Mandated by the Swiss Geological Survey (swisstopo) and the Swiss Federal Office of Energy (SFOE), we herewith provide an overview of completed and ongoing international research on mineral extraction from geothermal brines, with a focus on lithium, and the occurrence and distribution of currently available and publicly accessible data on lithium concentrations in deep aquifers in and around Switzerland.

Our compilation is based on the BDFGeotherm database and an extract of Nagra data from wells drilled until 2017. Currently, we do not have access to other potentially relevant hydrochemical data due to data restrictions. Additional information on the metal content of deep fluids likely exists in well reports of past and recent exploration projects (for example from the latest Nagra drilling campaign 2019-2022 and from various geothermal exploration projects) for which we do not have access authorisation yet.

This document has to be considered as a status report based on data available today.

2 Abstract

The production of geothermal energy coupled with the extraction of lithium or other critical metals from deep aquifers could provide an important economic incentive to scale up geothermal exploration and production in Switzerland. A review of the literature reveals that lithium, globally, has become one of the key critical raw materials needed for the energy transition, especially for the storage of energy. Therefore, the focus of lithium exploration has recently expanded to include geothermal brines, as an alternative to conventionally exploited hard rock occurrences or salar brines. Deep geothermal aquifers are known to occasionally contain significant concentrations of lithium. Although research pilot wells are well advanced (e.g. in Germany or the USA), no lithium is commercially produced from a geothermal well at industrial scale yet.

We have compiled 79 lithium concentrations from the publicly accessible wells in Switzerland deeper than 100 m. Lithium concentrations in the aquifers encountered are, with two exceptions, below 33 mg/l. Two wells in the Swiss Molasse Basin, at Pfaffnau and Berlingen, have elevated lithium concentrations of 82 mg/l and 144 mg/l, respectively. Both measurements originate from the Upper Muschelkalk aquifer. These concentrations are lower than the highest concentrations recorded so far in the Upper Rhine Graben (100-210 mg/l) or in several regions of Italy (up to 480 mg/l). The process of lithium enrichment in geothermal fluids at depth is yet poorly understood. Our data reveal that geothermal fluids with high TDS (total dissolved solids) values also have elevated lithium concentrations and are predominantly located in areas with high heat flow. In Switzerland, areas with high heat flow are located in the Basel and Lower Aare Valley regions as well as in the area of Lake Constance. An up-to-date heat flow map could provide useful indications for the exploration of metal-rich geothermal brines.

To better understand the spatial distribution and key parameters controlling the concentration of critical raw materials such as lithium in deep aquifers, and to provide a robust basis for further investigations, we propose the following measures: (i) update the data base with recent and not publicly available well data, (ii) repeat lithium concentration measurements at key sites with high concentrations but low confidence (if the well data or water samples are still accessible), (iii) analyse the geological setting (stratigraphy, reservoir properties, regional heat flow, local tectonics) in areas with high lithium concentrations to enhance the understanding of the process of lithium enrichment, (iv) establish a sampling and well testing protocol to guide the permitting authorities at Canton level and the operators of the future, federally-subsidised geothermal projects, to obtain comprehensive hydrochemical analyses of the deep fluids.

3 Lithium – a key energy transition element

3.1 Available data on lithium occurrences

The targeted clean energy transition, to reach the Paris Agreement 2-degree Celsius scenario at the global level, requires a series of so-called critical raw materials to manufacture batteries, electric cars, wind turbines, solar panels and many electronic components (European Commission 2022). These are, in particular, lithium, nickel, cobalt, manganese and graphite. Some of these critical raw materials are known to occur in geothermal brines (lithium (Li), beryllium (Be), boron (B), fluorine (F), magnesium (Mg), silicon (Si), phosphorus (P), cobalt (Co), germanium (Ge), strontium (Sr), antimony (Sb) and barium (Ba), Fig. 1). Among these, lithium is not the most critical one but the one with the fastest expected growth in demand. Global lithium demand is estimated to increase by a factor of four to eight by 2030 (Schmidt 2023). Nickel and cobalt demand are estimated to increase by a factor of 2 and 3 by 2050, respectively (Gregoir & van Acker 2022a). The energy technologies (i.e. batteries) will have a large share in this increase (e.g. Gregoir & van Acker 2022a, Hund et al. 2020, Fig. 2). However, the production of battery-grade lithium does not seem to the meet the increasing demand (Fig. 3). This could thus become a limiting factor for the global energy (i.e. mobility) transition (Schmidt 2023).

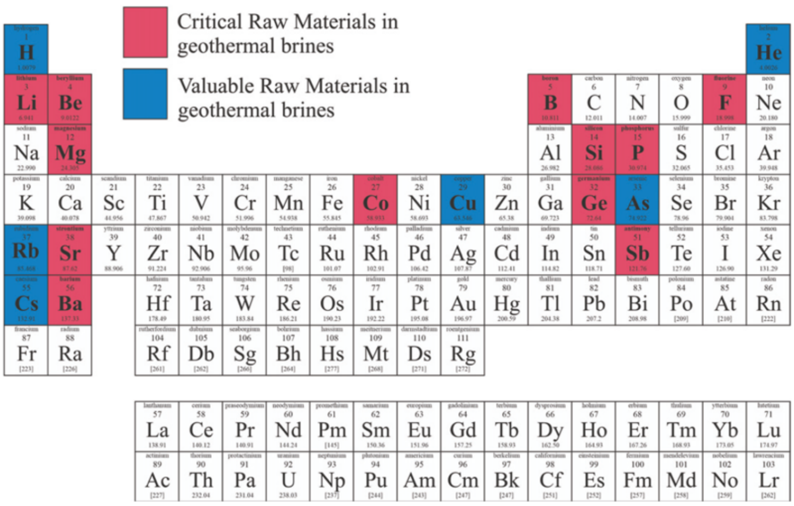

Fig. 1. Elements classified as critical by the European Commission (2022), which are known to occur in geothermal fluids (Goldberg et al. 2021).

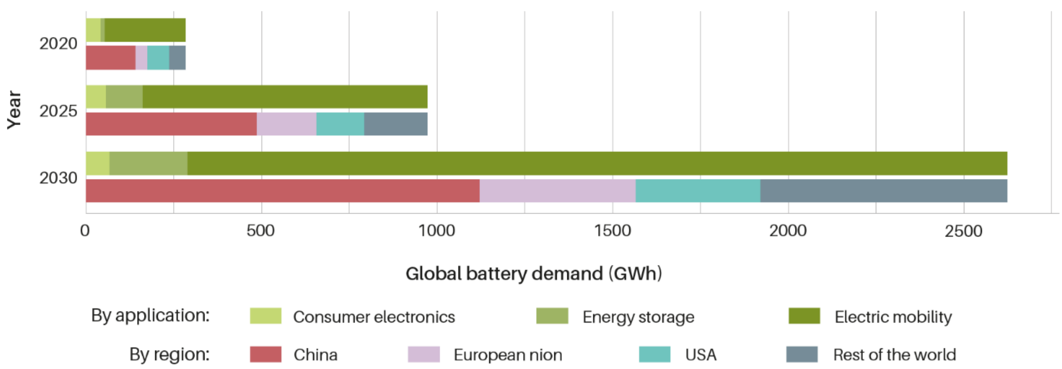

Fig. 2. Forecast of the global battery demand by application and region until 2030 (Lusty et al. 2022).

Following the urgency to find solutions to enable the energy transition and to minimise supply risks, the scientific, industrial and governmental communities are currently producing an increasing number of publications on the subject (e.g. Betrand et al. 2021, European Commission 2022, Goldberg et al. 2022a/b, Gregoir & van Acker 2022a/b, Kresse et al. 2022, Sanjuan et al. 2022, Schmidt 2023). A selection of the most relevant research is presented in the following chapters.

Although lithium is currently not mined in Europe, a huge growth in the battery production is foreseen with over 30 very large battery factories planned or already in construction (e.g. Goldberg et al. 2022b). Key driver for this growth is the European Green Deal (European Commission 2019) and the post-Brexit “Ten Point Plan for a Green Industrial Revolution” (BEIS 2020). The European Green Deal is aiming at facilitating the energy transition, fighting climate change and reducing environmental degradation by including an EU industry that will be globally competitive. This triggered numerous projects to explore for battery metals and materials in order to shorten supply chains (e.g. European Battery Alliance, EBA 2017). To achieve that, Europe will need significantly more new sources of supply of critical metals like lithium, nickel and cobalt.

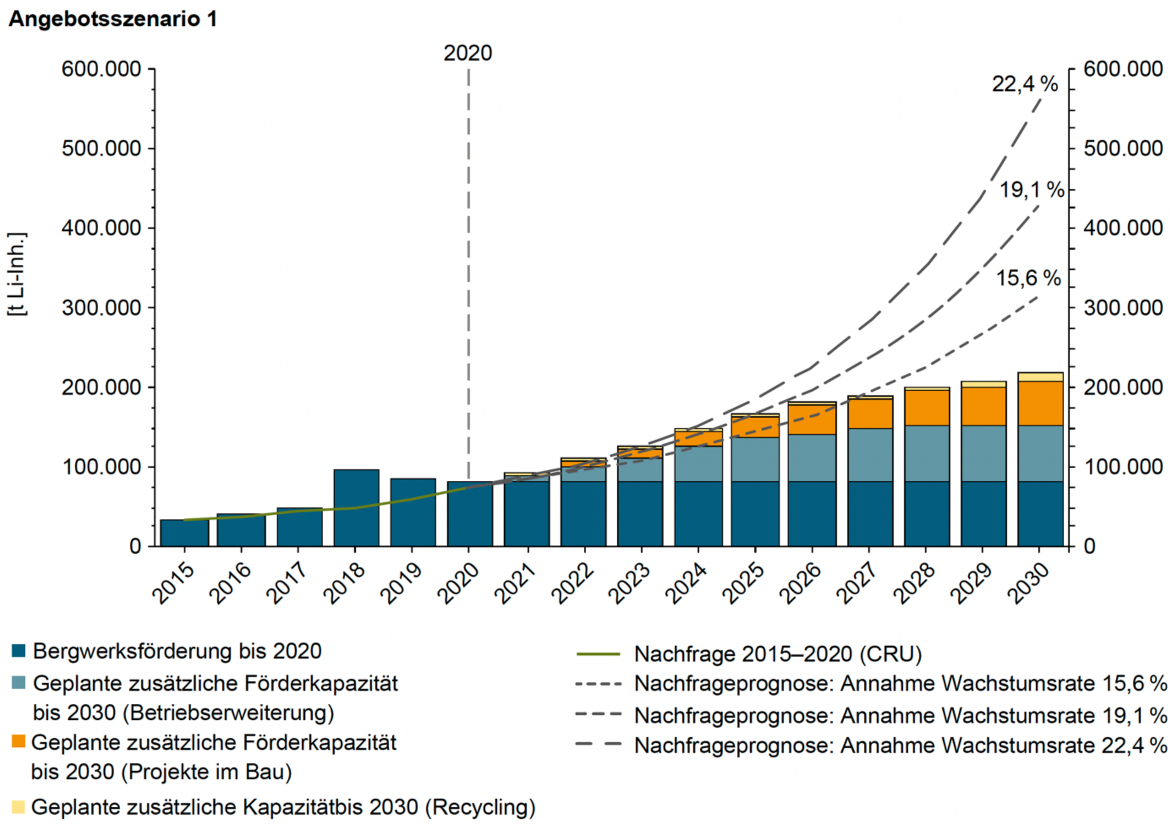

Fig. 3. Global development scenarios of lithium supply and demand until 2030 by the German Mineral Resources Agency DERA (Schmidt 2023). The coloured bars show the planned lithium production in tonnes. The three dashed lines show the estimated demand. Note that this scenario is calculated without any planned lithium production from geothermal brines. In the second scenario (the optimistic one) of this report, lithium production from brines is considered. That scenario yields a total production of about 360’000 t by 2030.

Metals have been mined in Europe for centuries. However, mining activities in Europe have declined significantly due to competitive advantages elsewhere. Reasons for that are cheaper labour, lower energy prices, less strict environmental protection regulations and a general higher acceptance of heavy industry. Regarding metals, the geology in Europe offers several opportunities in the metal mining districts in Sweden, Finland, Russia (Kola Peninsula), Ukraine, Poland, Germany, Romania, Bulgaria, Greece, Ireland, England, Spain, Portugal and Cyprus. In Europe, only low volumes of lithium, for ceramics and glass applications, are currently mined conventionally in Portugal. Historically, lithium has been used in industrial production processes to lower the melting temperature of glass and aluminium, used in applications such as the production of tritium for the nuclear arsenal, and used in the treatment of bipolar disorder (Bibienne et al. 2020). There are more than 10 new European lithium mining projects planned or announced: in France, Austria, Czech Republic, Germany, Finland, Portugal, Spain and Serbia (Goldberg et al. 2022b, Gregoir & Acker 2022b). There are also notable deposits in the UK and the Scandinavian countries. Currently, Europe is not extracting lithium due to economic and social factors, but not because of the geology. There is a lack of public acceptance for European lithium mining. As a consequence, investor confidence is low and financing insufficient.

3.2 Lithium for batteries

Energy storage by batteries is crucial for the energy transition for two main reasons: (1) it fuels electric vehicles, and (2) it is needed to store power from intermittent electricity generation obtained especially from solar photovoltaics and wind farms, including grid and decentralised operations (Fig. 4).

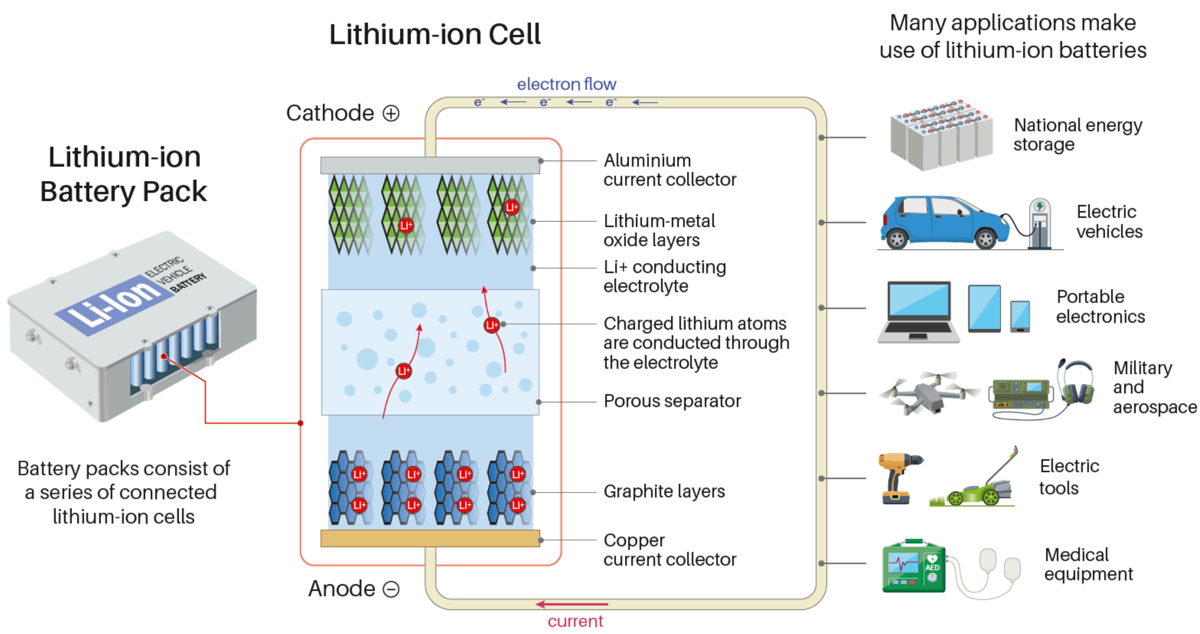

Fig. 4. Schematic diagram of a lithium-ion battery and cell, with examples of applications (Lusty et al. 2022).

The composition of lithium-ion batteries is a function of the selected materials (Fig. 4). The common and popular layered structured compounds include Li-Ni-Mn-Co oxide, Li-Ni-Co-Al oxide, $LiCoO_2$, spinel-structured compounds, such as $LiMn_2O_4$, olivine-structured $LiFePO_4$, complex orthosilicate-structured $LiMSiO_4$ (M = Mn^{2+}, Fe^{2+}, or Co^{2+}); and the recently described higher-current Li-Mn composite layered structures (Bibienne et al. 2020). These materials can be used as positive electrodes in lithium-ion batteries, in which graphite is a common negative electrode. Depending on the cathode type, the main constituents of a lithium-ion battery are lithium, cobalt, nickel, aluminium, iron, manganese and phosphate (e.g. Kresse et al. 2022).

The lithium-ion battery is a mature technology. However, many challenges remain to further improve its performance, recyclability and safety in the near future. Although markets for lithium have been small in the past, the rising demand driven by lithium-ion battery technology requires numerous new sources and is transforming a historically segmented supply chain into a much more integrated business. Before the battery-related increased interest on lithium in the 2000s, its global consumption reached only a few thousand tonnes per year (Arndt et al. 2017).

The rate of commercialisation of new batteries over the last decade has been much faster than anticipated. It is thus likely that a similar pace of innovation in battery technology will be kept in the future. Several potentially transformative next generation technologies will be of importance for energy storage and thus electromobility beyond 2030. This has related implications for demand for the specific mineral raw materials that will be required.

3.3 Lithium occurrences

3.3.1 Lithium-bearing minerals

Lithium occurs naturally in the continental crust with concentrations of ca. 20-60 mg/kg (Reich et al. 2022). The concentration of lithium in seawater is between 0.1 and 0.2 mg/l (Chubey et al. 2017). There are about 120 known mineral species containing lithium. 73% of these minerals are silicates, 19% are phosphates, and 8% are either carbonates, fluorides, oxides and hydroxides, borates or arsenites. The 124 recognised lithium-bearing mineral species occur mainly in four geological rock types (Grew 2020, Tab. 1):

(1) Lithium–Cesium–Tantalum (LCT) granitic pegmatites and associated metasomatic rocks,

(2) Highly peralkaline pegmatites,

(3) Metasomatic rocks not directly associated with pegmatites,

(4) Manganese deposits.

Tab. 1. Key lithium-bearing minerals and their major paragenesis (Grew 2020).

Mineral Name	Mineral Group	Chemical Formula	Number of Localities (Reported to Date)	Earliest Geologically Reported Age (Ma)	Major Paragenesis*
Spodumene	pyroxene	$LiAlSi_2O_6$	620	3,050	LCT pegmatite
Elbaite	tourmaline	$Na(Al_{1.5}Li_{1.5})Al_6(Si_6O_{18})$-$(BO_3)_3(OH)_3OH$	506	2,650	LCT pegmatite
Triphylite	triphylite	$LiFe^{2+}PO_4$	295	2,640	LCT pegmatite
Amblygonite	amblygonite	$LiAlPO_4F$	208	2,660	LCT pegmatite
Lithiophorite		$(Al,Li)Mn^{4+}O_2(OH)_2$	205	–	Supergene, manganese deposits
Montebrasite	amblygonite	$LiAlPO_4(OH)$	185	2,660	LCT pegmatite
Cookeite	chlorite	$(Al,Li)_3Al_2(Si,Al)_4O_{10}(OH)_8$	173	2,660	LCT pegmatite
Lithiophilite	triphylite	$LiMn^{2+}PO_4$	137	2,890	LCT pegmatite
Petalite		$LiAlSi_4O_{10}$	111	2,642	LCT pegmatite
Polylithionite	mica	$KLi_2AlSi_4O_{10}F_2$	86	3,000	LCT pegmatite (lepidolite), alkalic rocks
Ferrisicklerite	triphylite	$Li_{1-x}(Fe^{3+},Mn^{2+})PO_4$	73	2,890	LCT pegmatite
Sicklerite	triphylite	$Li_{1-x}(Mn^{2+},Fe^{3+})PO_4$	53	2,890	LCT pegmatite
Neptunite	neptunite	$KNa_2LiFe^{2+}{}_2Ti_2Si_8O_{24}$	50	1,332	Alkalic rocks, natrolite veins
Holmquistite	amphibole	$\square Li_2(Mg_3Al_2)Si_8O_{22}(OH)_2$	37	2,660	Metasomatic contact of LCT pegmatites
Tainiolite	mica	$KLiMg_2Si_4O_{10}F_2$	37	1,750	Alkalic rocks
Rossmanite	tourmaline	$\square(LiAl_2)Al_6(Si_6O_{18})$-$(BO_3)_3(OH)_3OH$	35	2,640	LCT pegmatite
Tavorite	amblygonite	$LiFe^{3+}PO_4(OH)$	34	1,702	LCT pegmatite

* LCT = Li–Cs–Ta

3.3.2 Lithium deposits

Lithium exploration traditionally focussed on the two main types of economic lithium deposits, granitic pegmatites and lacustrine brines (Fig. 5). Recently, activities expanded into previously uneconomic deposits such as lacustrine sediments and oil field brines (Arndt et al. 2017). Whereas production numbers are more or less consistent and reliable, there are large inconsistencies in the estimates of the volumes of raw material occurrences. Incomplete information and deficient assessment of potential occurrences have led to a great range of lithium resources estimates ranging from 14 to 64 Mt according to compilations published between 2008 and 2016 (Kesler et al. 2012, Arndt et al. 2017 and references therein).

The natural occurrence of lithium in potentially economic quantities is currently limited to the following three deposit types (Bowell et al. 2020):

(1) Hard rock deposits: granitic pegmatite deposits and their associated metasomatic rocks.
Key deposit types are the lithium-cesium-tantalum (LCT) pegmatites with a bulk lithium content of 0.58-1.18 wt% and spodumene as the major lithium-bearing mineral.

(2) Soft rock deposits: volcanic clay deposits.
Volcanic tuffs containing the lithium-rich clay mineral hectorite or other lithium-clays have a bulk lithium content of 0.17-0.24 wt%.

(3) Dissolved deposits (brines): salar evaporites (lacustrine brines) and geothermal fluids.
Continental brines in salars typically have a bulk lithium content of 0.01-0.18 wt%, whereas geothermal brines and oilfield brines have 0.01-0.03 wt% and 0.01-0.05 wt%, respectively.

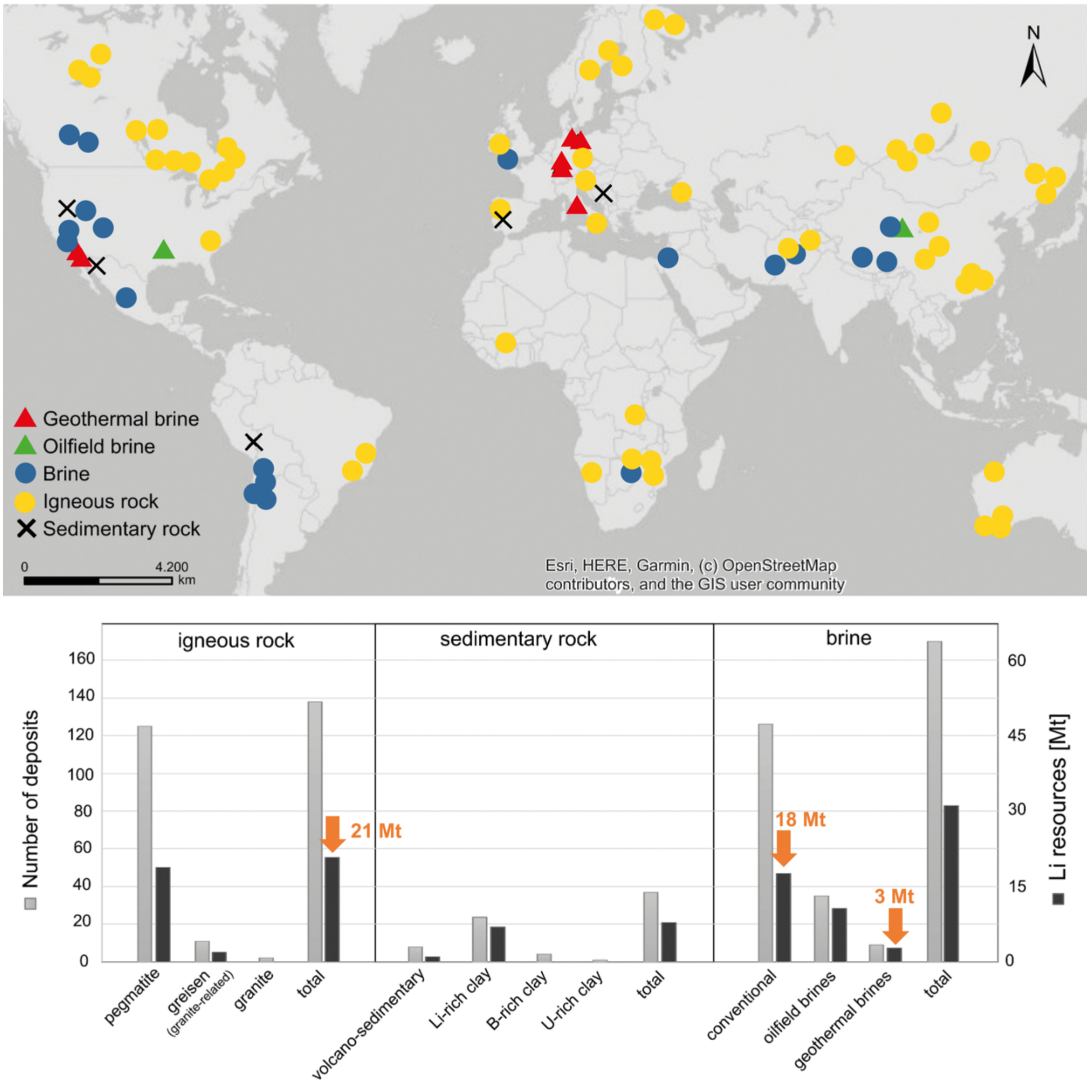

Fig. 5. Global lithium deposits and resource distribution between different deposit types (Reich et al. 2022). Note that the estimated lithium resources from geothermal brines (3 Mt) is 7 times smaller than lithium from igneous rocks (21 Mt), and 6 times smaller than from conventional brines (ca. 18 Mt).

Spodumene-bearing pegmatites are the most important and relatively easily exploitable lithium deposits. They account for about 40% of the known global resources. Generally, LCT pegmatites have the highest lithium grades, best represented by very large deposits such as Greenbushes (Australia, 1.091 wt% lithium) and Pilgangoora (Australia, 0.580 wt% lithium). Lithium-rich clay type deposits have medium grade with the largest and richest deposits represented by Thacker Pass (USA, 0.236 wt% lithium) and Sonora (Mexico, 0.229 wt% lithium). Lithium-rich continental brines (salar deposits) hold the world's largest lithium resources (about 60% of the known global resources), but they are more difficult to exploit. These brine deposits tend to have the lowest grades compared to the other deposit types. High-grade brine deposits are located at Zhabuye (China, 0.1 wt% lithium) and Atacama (Chile, 0.184 wt% lithium). In recent years, other currently economic volcanogenic deposits were discovered such as the Falchani, composed of felsic lithium-rich tuffs (Peru, 0.296 wt% lithium), and the Jadar, where lithium is hosted in a sodium-lithium boron silicate hydroxide named Jadarite (Serbia, 0.836 wt% lithium). See Tab. 2 for an overview. Tab. A1 lists major hard-rock lithium minerals with their average lithium content.

Total global lithium resources are currently estimated at less than 100 Mt (Ambrose & Kendall 2020) with Bolivia, Argentina, Chile, USA and Australia having the largest resources world-wide (21 Mt, 19.3 Mt, 9.6 Mt, 7.9 Mt, and 6.4 Mt, respectively). Today, the world's major lithium producers are Chile, Australia, Argentina, China and the USA (Fig. 6).

Tab. 2. Main, global lithium deposits, aggregated according to their deposit type (Bowell et al. 2020)

Deposit	Type	Location	Main Owner	Li (Kt)	Grade (wt% Li)
Greenbushes	Pegmatite	Greenbushes (Australia)	Tianqi Lithium	943	1.091
Wodgina	Pegmatite	Pilbara (Australia)	Mineral Resources	826	0.543
Earl Grey	Pegmatite	Goldfields (Australia)	Kidman Resources & SQM	658	0.697
Pilgangoora	Pegmatite	Pilbara (Australia)	Pilbara Minerals	628	0.580
Grota do Cirilo	Pegmatite	Minas Gerais (Brazil)	Sigma Lithium	293	0.641
Whabouchi	Pegmatite	Quebec (Canada)	Nemaska Lithium	220	0.604
Arcadia	Pegmatite	Harare (Zimbabwe)	Prospect Resources	164	0.608
Tanco	Pegmatite	Manitoba (Canada)	Sinonime Rare Metals	110	1.180
Atacama	Brine	Atacama (Chile)	SQM; Albermarle	6,300	0.184
Uyuni	Brine	Oruro and Potosí (Bolivia)	COMIBOL	3,600	0.045
Zhabuye	Brine	Tibet (China)	Tibet Shigatse & Tianqi	1,500	0.100
Centenario	Brine	Salta (Argentina)	Eramet	921	0.045
Hombre Muerto	Brine	Catamarca (Argentina)	Livent	835	0.071
Olaroz/Cauchari	Brine	Jujuy (Argentina)	Orocobre	345	0.053
Cauchari	Brine	Jujuy (Argentina)	Lithium Americas & Exar	282	0.069
Maricunga	Brine	Atacama (Chile)	Minera Salar Blanco	269	0.117
3Q	Brine	Catamarca (Argentina)	Neo Lithium	243	0.079
Rincon	Brine	Salta (Argentina)	Argosy Minerals	203	0.032
Clayton Valley	Brine	Nevada (USA)	Pure Energy Minerals	41	0.012
Sonora	Li-Clay	Sonora (Mexico)	Bacanora & Ganfeng	845	0.229
Thacker Pass	Li-Clay	Nevada (USA)	Lithium Americas	582	0.236
Rhyolite Ridge	Li-clay	Nevada (USA)	Ioneer Resources	209	0.170
Falchani	Li-Tuff	Puno (Peru)	Plateau Energy Metals	146	0.296
Jadar	Jadarite	Jadar (Serbia)	Rio Tinto	435	0.836

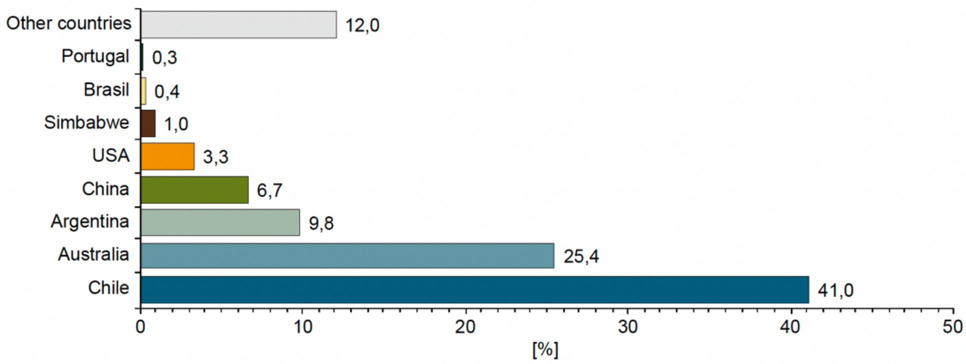

Fig. 6. Percentage distribution of global lithium reserves for the year 2021 (Schmidt 2023, usgs.gov)

3.3.3 Lithium data from Europe (FRAME project)

In the framework of the GeoERA Raw Materials project, the FRAME project (2018-2021) aimed at "Forecasting and Assessing Europe's Strategic Raw Materials needs" (geoera.eu/projects/frame2). The project built on previously developed pan-European and national databases and expanded the strategic and critical raw materials knowledge through a compilation of mineral potential and metallogenic areas of critical raw materials resources in Europe. The mineral resources targeted will have to be extended beyond the current EU critical raw materials list and include also minerals and metals (e.g. lithium, copper, and manganese) that are strategic for the European industry. Work package 3 produced a series of “Critical and Strategic Raw Materials Map of Europe”, among those also a “Favourability ap for lithium mineralisation in Europe” (Fig. 7). These maps do not include metals in geothermal brines.

According to Bertrand et al. (2021), there seems to be a certain potential for lithium mineralisations in solid rocks (mainly pegmatites) in the Alps (Fig. 7). These maps document several sites with lithium-bearing minerals in crystalline rocks in the Swiss Alps (mainly Grisons, Ticino and Valais Cantons). However, while our group’s Resources Information System (map.georessourcen.ethz.ch, Fulda et al. 2018) does not explicitly list sites with lithium occurrences, it lists pegmatites that could point to potential enriched occurrences of this metal.

A recent comprehensive overview of key lithium deposits in solid rocks of Europe is given by Gourcerol et al. (2019).

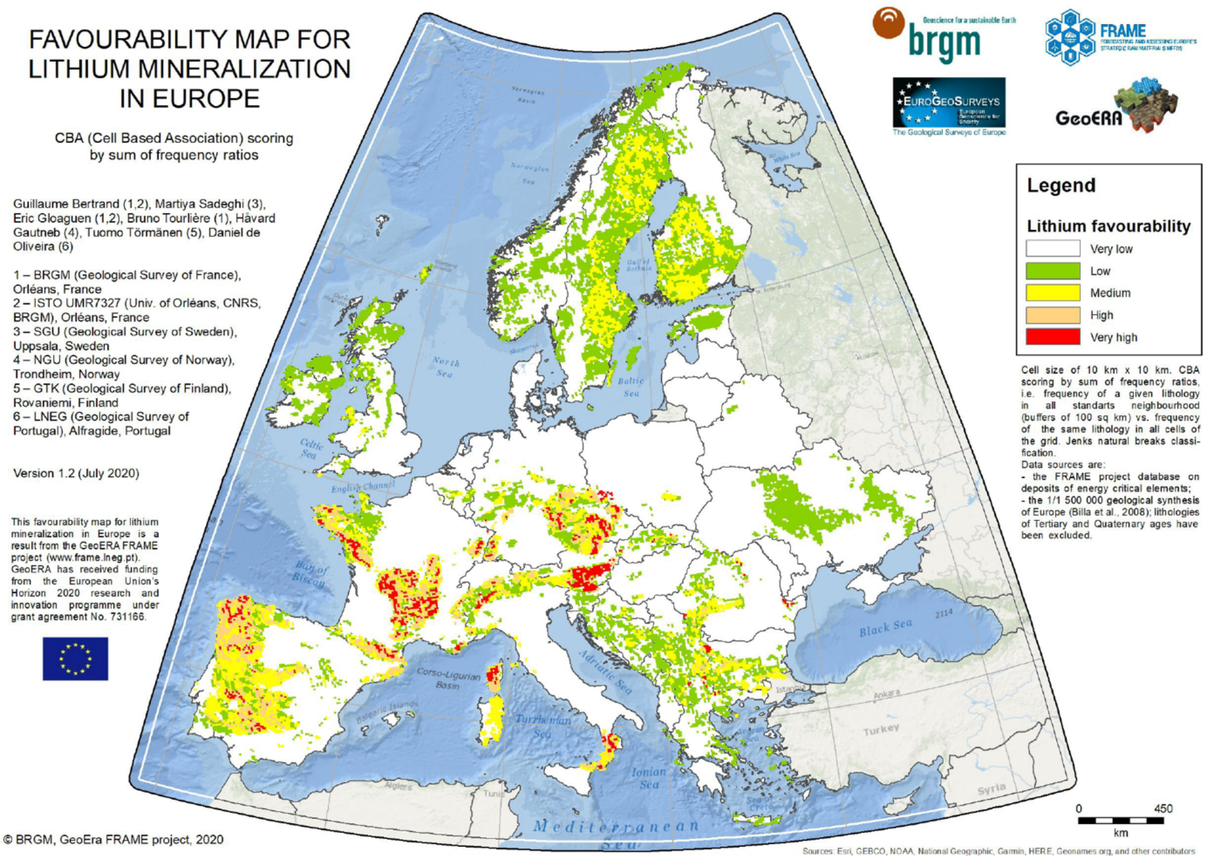

Fig. 7. Favourability map for lithium mineralisations in Europe (Betrand et al. 2021).

3.4 Lithium extraction from geothermal brines

Since the future demand of lithium is expected to increase dramatically, the extractive industry is called to find solutions to secure the supply chain. At the time being, it appears obvious that the recycling industry (e.g. of Li-ion batteries) cannot significantly cover the demand alone by 2050 since most recycling technologies are still being developed and investigated only at lab-scale (Ambrose & Kendall 2020). New, unconventional lithium sources and extraction methods are therefore needed. One potential source could be geothermal brines. The chemical composition of the geothermal brines is dependent of the source rocks and thus differs between geological provinces. Conventionally mined brines and typical geothermal brines have similar concentrations of total dissolved solids of about 100-330 g/l (e.g. Reich et al. 2022). Furthermore, they both have slightly acidic to slightly alkaline pH and high concentrations of major cations and anions. Lithium concentrations in most geothermal fluids vary between 20 and 1’750 mg/l (Reich et al. 2022 and references therein).

Although the theoretical potential for raw material extraction from geothermal brines is very high, hardly any plant in the world is currently extracting critical raw materials at industrial scale (e.g. Goldberg et al. 2022a/b). Lithium-rich geothermal brines are characterised by complex chemistry, high salinity, and high temperatures, which pose unique challenges for economic lithium extraction (Stringefellow & Dobson 2021). Besides finding lithium-rich geothermal fluids in a volumetrically quantifiable geothermal reservoir (aquifer), the main challenge is to find suitable methods for the selective extraction of elements. Processes must be found to extract elements from a complex saline solution with the highest possible degree of purity, with simultaneously operating a geothermal powerplant, with both processes at maximum efficiency and speed.

Instead of applying evaporation techniques, as used for lithium extraction from continental brines, so-called Direct Lithium Extraction (DLE) methods are developed mainly for extraction from geothermal brines (e.g. Goldberg et al. 2022a). These methods use various chemical and physical techniques to extract lithium from brines. They have the advantage that they are essentially closed-loop systems and thus allow for a more sustainable lithium production compared to current evaporative brine and hard rock mining in terms of land use, water use, time to market with lithium products, and carbon intensity of operations (BGS 2020, Warren 2021).

For (direct) lithium extraction, a number of methods indicate a high potential, at least on a laboratory scale (Liu et al. 2019, Goldberg et al. 2022a, Reich et al. 2022). These are (1) concentration and precipitation, (2) organic sorbents, (3) inorganic molecular sieve ion-exchange adsorbents, (4) electrochemical methods, (5) membrane separation technologies and (6) solvent separations.

The most studied and technologically advanced method for direct lithium extraction from brines is adsorption by metal oxides and hydroxides. Solvent extraction of lithium from brines using lithium-selective solvents and sorption using organic polymer sorbents, including metal-imprinted polymers, are early-stage technologies that seem to be promising. Membrane-based processes are largely used for removing water or interfering ions, rather than for the direct extraction of lithium. Processes based on precipitation and common ion-exchange resins can extract lithium from brines but are not specific to lithium and therefore are not considered practical for economical lithium extraction from geothermal brines, which have very complex chemistry (for more details see for example Stringefellow & Dobson 2021, Goldberg et al. 2022a).

In a typical combined power generation and lithium extraction plant, the common extraction steps are as following: the geothermal brine is pumped from a depth of about 2-5 km. Steam is generated in a heat exchanger that will run a turbine to produce electricity. The brine is pumped to an extraction plant where the pressure has to be released. A risk at this step could be that heavy precipitation of dissolved impurities will block pumps, pipes and valves. Impurities and other metals like Zn, Mn, etc. need to be removed from the brine in most cases. From this pre-purified brine, lithium is extracted mainly as lithium chloride (LiCl) and then needs further processing to lithium carbonate (Li_2CO_3) or lithium hydroxide (LiOH). For this extraction process, there is no standard procedure established yet. After the heat exchange, the brine is usually reinjected into a well. This carries the potential of aquifer pollution as several alkaline impurities were added to the brine by the above chemical treatment during lithium extraction.

4 Lithium extraction from geothermal brines in Europe

4.1 Overview

There are several ongoing investigations on how and whether lithium could be economically extracted from deep geothermal brines in Europe. Relevant overviews are presented for example in Sanjuan et al. (2022) or Goldberg et al. (2021, 2022a/b). There are six areas (Fig. 8) that show high lithium concentrations in geothermal brines (125-480 mg/l) in Germany, France, Italy and the UK (Sanjuan et al. 2022). The European Geothermal Energy Council estimated a potential for the production of geothermal lithium for even more areas (Fig. 9).

Defining a benchmark lithium concentration in geothermal brines, that would indicate at which point extraction can be technically and economically feasible (cut-off value), depends on many factors (see in-depth discussion on project examples from Germany in Goldberg et al. 2022b). In contrast to conventional mining projects, in which several hundred exploration wells are drilled to assess the properties of the deposit, the metal extraction from geothermal brines is associated with comparatively large uncertainties mainly due to the limited number of exploration wells available. For example, the size and the longevity (e.g. continuity of sufficient flow rates) of the geothermal reservoir is poorly known to a large extent. As the primary focus of geothermal exploration is the extraction of heat, potentially occurring metals (i.e. lithium) are representing just a co-product. Therefore, it is unclear how to estimate an independent cut-off value for the lithium concentration. The lithium extraction projects planned in the German and French Upper Rhine Graben area are located at well sites with lithium concentrations in geothermal fluids exceeding 150 mg/l. This gives an indication of the magnitude of the concentrations required.

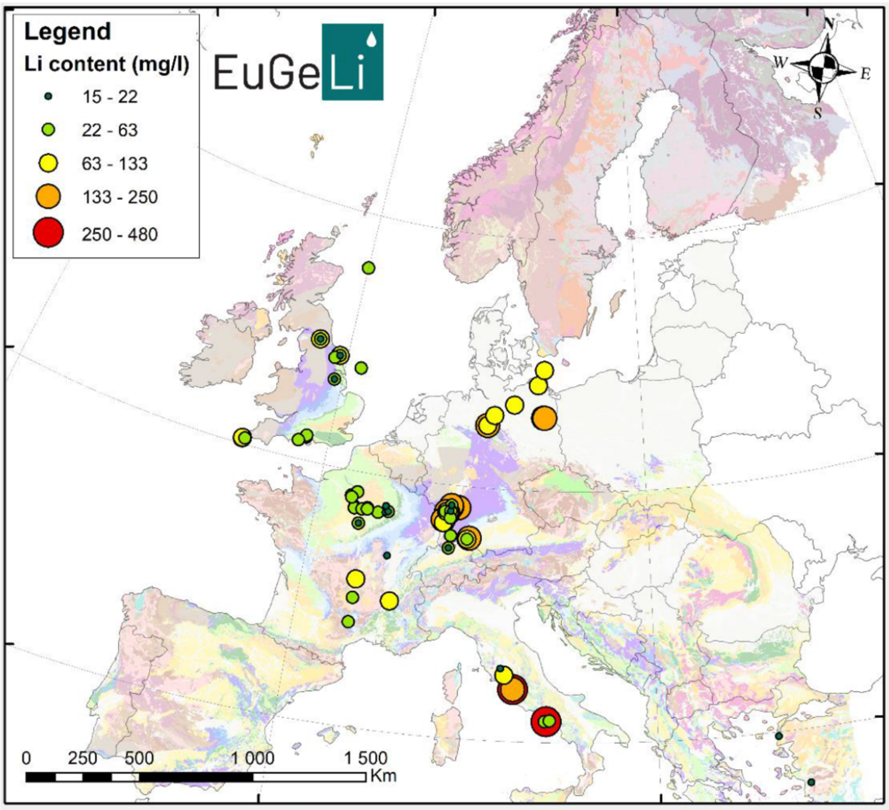

Fig. 8. Distribution of well sites with concentrations of lithium in geothermal brines in Europe (Stringfellow & Dobson 2021).

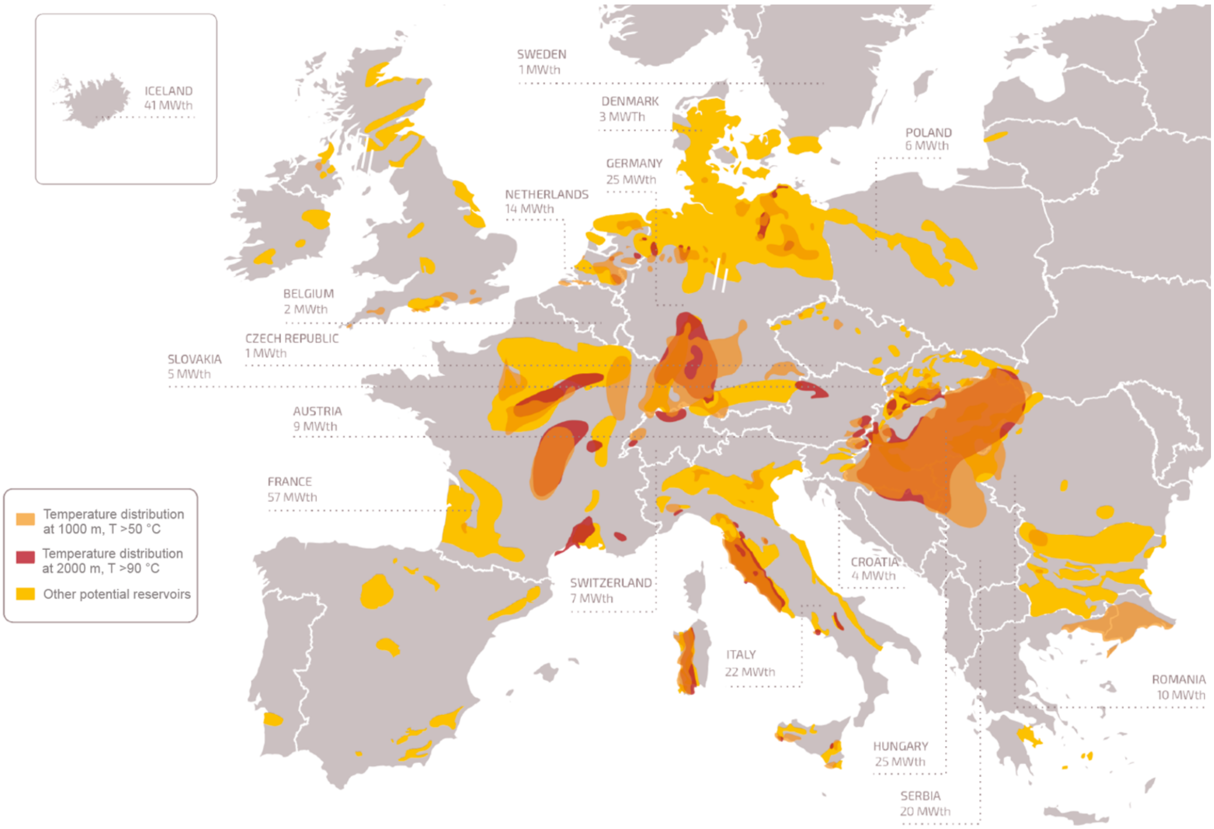

Fig. 9. Areas with geothermal lithium potential according to the European Geothermal Energy Council (EGEC 2023). This report does not provide any detailed information on the data used to compile this figure. Thus, we do not know how the highlighted areas were defined.

4.2 European Union research projects

4.2.1 Reflect

The ongoing Reflect project aims at “Redefining Geothermal Fluid Properties at Extreme Conditions” (reflect-h2020.eu). It will determine the effect of relevant fluid properties and reactions in order to enhance predictive geochemical modelling and thus the energy exploitation and lifetime of geothermal power plants. Among the several project tasks and products, the establishment of the “fluid atlas” is the most important one regarding lithium extraction from brines. The atlas (reflect.uni-miskolc.hu/efa) compiles information on geothermal fluid properties across Europe together with the corresponding geological setting of the reservoir and was published online in 2022.

4.2.2 CRM geothermal

The ongoing CRM geothermal project is a two-year EU project that started in spring 2022. The topic is “raw materials from geothermal fluids: occurrence, enrichment, extraction” (crm-geothermal.eu). To assess overall supply potential, CRM geothermal will establish an overview over the potential for raw materials in geothermal fluids for a large range of CRM elements across the EU and third countries. The potential of different geological settings for combined extraction will be evaluated. Extraction/separation techniques exist but need to be adapted to the challenging conditions of such systems (high temperature, pressure and salinity). Combinations of materials and flow schemes will be assessed at lab scale to optimise systems for different geothermal settings and CRM. A modular, mobile plant will be developed and deployed at existing geothermal sites to conduct pilot studies, investigating upscaling and system integration.

4.3 Upper Rhine Graben (Germany & France)

4.3.1 Overview

The Upper Rhine Graben extends along the Rhine River between the Jura fold-and-thrust belt in the Basel area (CH) and the Taunus Mountain range near Wiesbaden/Mainz (D). The geothermal gradient in this graben is significantly higher-than-average with temperatures of 170 °C at about 3 km depth. The up to 4-5 km thick graben infill (sediments) and the underlying, fractured crystalline basement can have excellent reservoir properties (e.g. Frey et al. 2022).

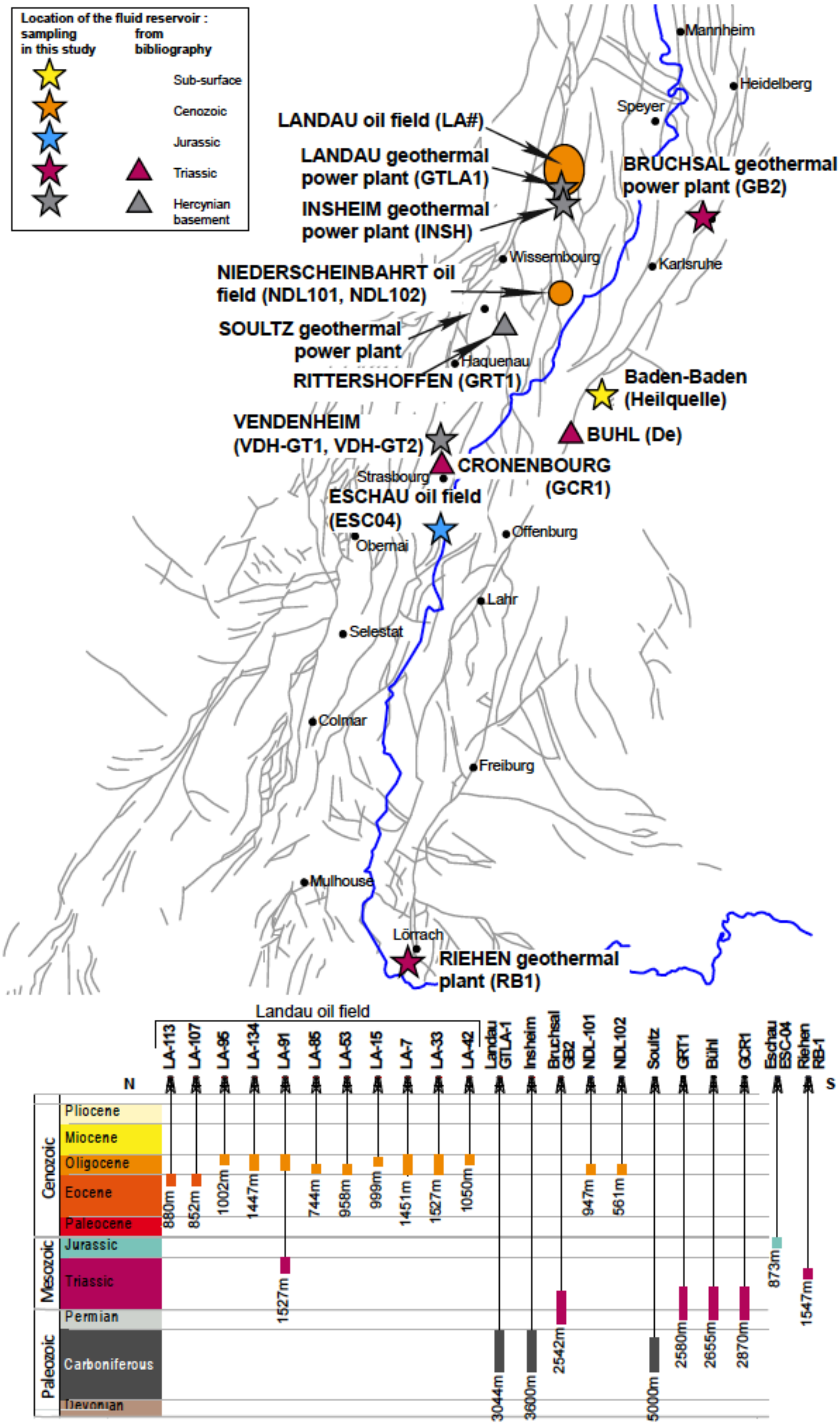

Fig. 10. Location of deep wells and the stratigraphic position of the geothermal reservoirs in the Upper Rhine Graben (Sanjuan et al. 2016). Note that this map is from 2016 and does not show all geothermal projects planned/operating today.

Fluids from deep geothermal wells are described as Na-Cl water type, with a pH value around 5, and total dissolved solids of ca. 100 to 110 g/l (e.g. Sanjuan et al. 2016). The fluids are interpreted to be derived from multiple origins with a mixing of primary marine brines and water of meteoric origin. Lithium is locally enriched in fluids and stored mainly in the Triassic Muschelkalk and Buntsandstein or fractured crystalline basement aquifers (Fig. 10). Given the comparatively high lithium concentrations (100-210 mg/l, e.g. Sanjuan et al. 2016, Fig. 11, Fig. 12) and the large volumes of the geothermal fluids, the region appears to have a high potential for lithium extraction under the current market conditions (Goldberg et al. 2022b).

More details and good overviews on current exploration and research projects on the Upper Rhine Graben geothermal-related reservoir geology are given for example on the website geothermie.de, in Frey et al. (2022), Goldberg et al. (2022b) , Sanjuan et al. (2016, 2022) and in Fig. 13.

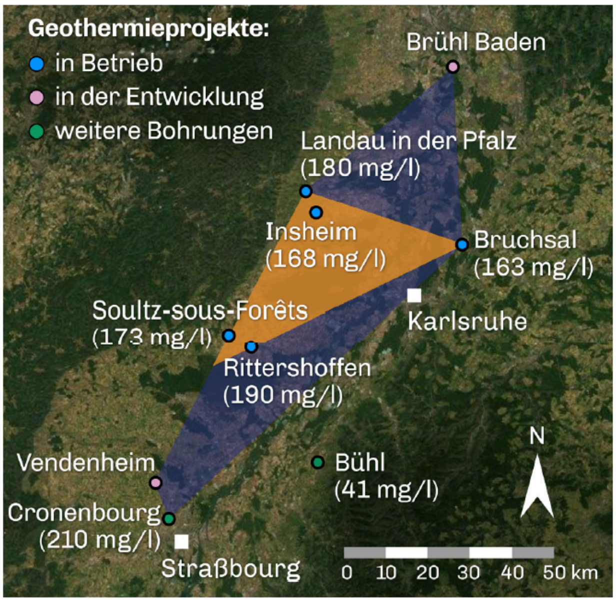

Fig. 11. Overview map of geothermal wells in the Upper Rhine Graben with high lithium concentrations. Orange polygon: the "lithium triangle", characterised by economically valuable lithium concentrations. The blue area includes the geothermal well sites with lithium contents above 150 mg/l (Kölbel & Schneider 2021).

Standort	Betreiber	Reservoir Formation	Anzahl der Bohrungen	Betrieb seit	Fließrate (L/s)	Lithiumgehalt (mg/L)
Landau (Pfalz)	ecoprime	Granit	2	2007	40	180
Insheim	Natürlich Insheim*	Granit	2.5	2012	70	168
Bruchsal	EnBW	Sedimentgestein	2	2011	28	163
Soultz-sous-Forêts	ÉS	Granit	4	2008	30	173
Rittershoffen	ÉS	Granit	2	2016	80	190

Fig. 12. List of operating geothermal well sites with substantial lithium concentrations at aquifer depth in the Upper Rhine Graben (Kölbel & Schneider 2021).

4.3.2 Vulcan Energy Resources (Germany)

The German-Australian company Vulcan Energy Resources (Vulcan Energie Ressourcen GmbH, v-er.eu) holds several exploration licences in the Upper Rhine Graben and plans commercial extraction of lithium from geothermal brines in 2024 (Goldberg et al. 2022a). The main focus initially was on the Ortenau and Taro fields with targets in the Muschelkalk, Buntsandstein and uppermost basement aquifers. Currently, several 3D seismic surveys are planned and will likely lead to new discoveries.

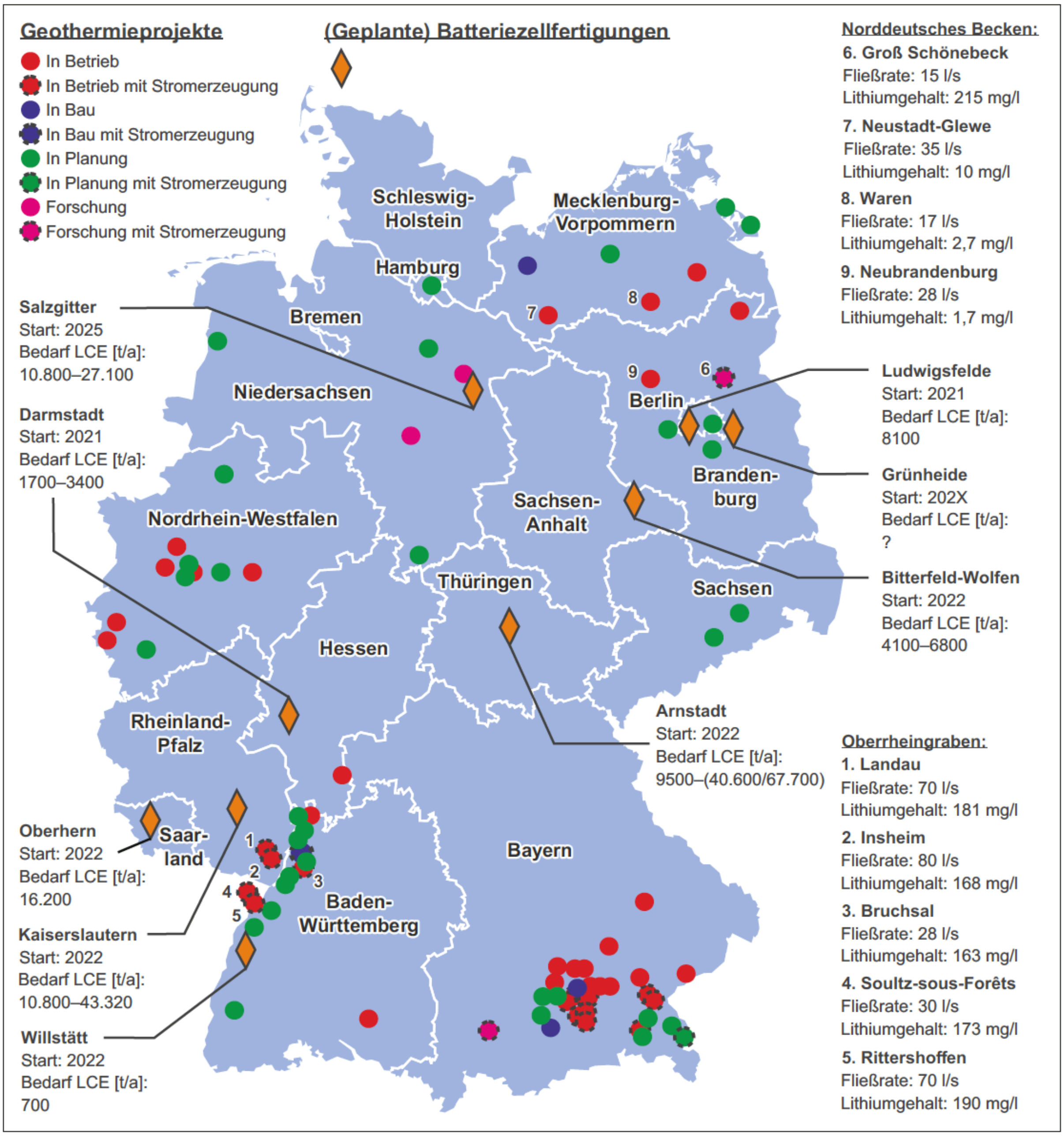

Fig. 13. Geothermal well locations and planned battery cell production sites in Germany (Goldberg et al. 2022b).

4.3.3 Li⁺Fluids research project (Germany)

The Federal Institute for Geosciences and Natural Resources (BGR) coordinates the research project Li⁺Fluids that runs 2021-2024 (bgr.bund.de/li+fluids). The project will investigate the potential for the extraction of lithium from geothermal fluids in Germany. It includes several subprojects to precisely assess the economic, geological and technical conditions for lithium extraction from geothermal brines. It is planned to evaluate the extraction processes known to date, to investigate lithium release rates from rocks at depth and to perform a utility value analysis for the extraction of lithium from geothermal brines.

The research is co-sponsored by BMWi and is carried out by the Fraunhofer Einrichtung für Energieinfrastruktur und Geothermie (IEG) and the Fraunhofer-Institut für Umwelt-, Sicherheits- und Energietechnik (UMSICHT).

4.3.4 EuGeLi (EU)

The EuGeLi (European Geothermal Lithium Brines) project was carried out 2019-2021 and aimed at providing Europe with lithium extracted from geothermal brines located at the French/German border (eitrawmaterials.eu/project/eugeli, eramet.com/eugeli-project). The project was co-funded by the European Union and carried out by a research consortium with the member institutions and companies ERAMET IDeas, BASF Netherlands, BRGM, Chimie ParisTech, EIfER, Electricité de Strasbourg, IFPEN, VITO and Vrije Universiteit Brussel.

An innovative lithium extraction process could be successfully developed by ERAMET and IFPEN and has proven to suitably extract lithium from geothermal brines. At the Rittershofen geothermal power plant, the first kilograms of battery-grade lithium carbonate from a geothermal brine could be produced.

4.3.5 UnLimited (Germany)

The research project UnLimited (geothermal-lithium.org) is carried out by a partner network consisting of EnBW, Karlsruher Institut für Technologie (KIT), Universität Göttingen, Bestec and Hydrosion. It is funded by the German Bundesministerium für Wirtschaft und Energie and aims at developing and testing a process to extract lithium from deep geothermal aquifers in Germany. A major focus of the investigation is the selection of particularly qualified lithium-selective adsorbents. In addition to the material properties, the main selection criteria are environmental compatibility during production, use and recycling or disposal. Suitable adsorbents will be tested at selected test sites including the Bruchsal geothermal power plant, which is operated by EnBW Energie Baden-Württemberg AG together with Stadtwerke Bruchsal since 2010.

4.3.6 GEOLITH (France)

The French start-up GEOLITH (geolith.fr) has built a pilot demonstrator for extracting lithium from brines (geothermal water, oil waters and salt brines) which operates for tests in Alsace. In 2019, GEOLITH obtained the support from ADEME (French Environment and Energy Management Agency) for its lithium capture research and development program in collaboration with MinesParisTech. Further tests of the direct lithium extraction are planned at the geothermal pilot plant at the United Downs Deep Geothermal Project in Cornwall (UK), in collaboration with UK-based GeoCubed, a joint venture between Cornish Lithium Limited and Geothermal Engineering Limited (GEL).

4.3.7 Lithium de France

Lithium de France (lithiumdefrance.earth) was founded by the French Averne group in 2020 and is exploring for a combined usage of geothermal heat and lithium extraction in the northern Alsace region. They have a five-year exploration licence for a 170 km^2 area in which 3D seismic measurements started in September 2022.

4.4 Other projects, companies, consortia and potential lithium-rich areas

4.4.1 Geothermal research platform Gross Schönebeck (Germany)

The GFZ geothermal research platform Gross Schönebeck is situated northeast of Berlin on the southern edge of the North German Basin. Two research wells form a geothermal doublet and give access to water-bearing horizons at depths between 3.9 and 4.4 km and temperatures of 150 °C. They are used as an in-situ laboratory for investigating deep sedimentary structures and fluids under natural conditions. The concentration of lithium at the Rotliegend aquifer is 215 mg/l, locally even 400 mg/l (e.g. Goldberg et al. 2022b).

4.4.2 Southwestern German Molasse Basin

In the southwestern German Molasse Basin, just northeast of the Lake Constance, there are two major thermal aquifers of interest for production of geothermal energy, the Upper Jurassic (Malm) limestone and the Middle Triassic Muschelkalk limestone (e.g. Stober 2014). Stober (2014) compiled and re-analysed more than 200 water samples from deep wells in the area. She could show that lithium concentrations generally are low and are in the order of <1 mg/l. But in the Muschelkalk limestone, concentrations are higher and reach up to 162 mg/l.

4.4.3 Brine Mine (Germany & Chile)

The BrineMine project is a German-Chilean multidisciplinary research project carried out by research and industry partners (geothermics.agw.kit.edu/brinemine.php). The project focusses on development of strategies for raw material and water extraction from geothermal springs in Chile. The two key topics are (1) determination of the economic potential of thermal waters as a raw material resource and (2) pre-treatment of thermal waters prior to raw material extraction (Goldberg et al. 2021).

The application of the developed prototype takes place in two steps, first at the geothermal power plant Insheim (Germany) in the Upper Rhine Graben (operated by Pfalzwerke geofuture GmbH), and afterwards in Chile. This three-year research project is funded by the German Federal Ministry of Education and Research. The project is led by the Fraunhofer Institute ISE (Institute for Solar Energy Systems). Further partners are Karlsruhe Institute of Technology (KIT), the Andean Geothermal Centre of Excellence (CEGA) at the Universidad de Chile, SolarSpring membrane solutions, Geothermie Neubrandenburg (GTN), CSET, GTN Latin America and Transmark Renewables. In the framework of this study, Goldberg et al. (2021) compiled a preliminary global hydrochemistry database containing about 10’000 water sample sites.

4.4.4 Zinnwald Lithium Project (Germany)

Zinnwald is an integrated lithium project focusing on hard rock mining at Zinnwald in the Erzgebirge in northeastern Germany (zinnwaldlithium.com). The Zinnwald deposit was historically mined for tin (Sn) and tungsten (W). Lithium will soon be mined from leucogranite deposits rich in the lithium mica Zinnwaldite (e.g. Dittrich et al. 2020).

4.4.5 Wolfsberg Lithium Project (Austria)

Wolfsberg is a hard rock lithium deposit located 270 km southwest of Vienna (Austria). European Lithium is a mining, exploration and development company running the Wolfsberg Lithium Project and plans to conventionally mine the deposit by underground excavation (europeanlithium.com).

4.4.6 CNR, Altamin & Vulcan Energy (Italy)

The National Research Council of Italy (CNR, Consiglio Nazionale delle Ricerche) has published an overview of the lithium occurrences in Italy in 2022 (Dini et al. 2022). The study evaluates all known and potentially occurring lithium-bearing rocks and fluids. As highlighted in Fig. 14, the largest lithium concentrations in geothermal brines are known from the high heat flow (>100 mW/m^2) geothermal systems of Tuscany and Lazio, as well as from Campania.

The Australian mineral exploration company Altamin has two exploration licences in central Italy, 50 km northwest of Rome, in the Cesano geothermal area located in the Baccano-Cesano caldera, just next to a license held by Vulcan Energy (Richter 2022a/b). Among 12 wells deeper than 3.2 km, the test well Cesano-1 yielded lithium concentrations of 350-380 mg/l from an aquifer at 1’390 m depth and with total dissolved solids (TDS) of 356’000 mg/l (Dini et al. 2022).

4.4.7 Cornish Lithium (UK)

Cornish Lithium (cornishlithium.com) is involved in several projects aiming at lithium extraction from brines in Cornwall (UK). Most advanced is the pilot lithium extraction plant that is being built in the United

Downs Deep Geothermal Project, in collaboration with Geothermal Engineering Limited through the joint venture GeoCubed. That pilot plant will use Direct Lithium Extraction (DLE) technology to recover lithium from geothermal fluids at 5.2 km depth in granitic rocks. In a well in the area of the South Crofty mine, at 690 m depth in the Carnmenellis granite, geothermal fluids yield a lithium concentration of 125 mg/l (Edmunds et al. 1985).

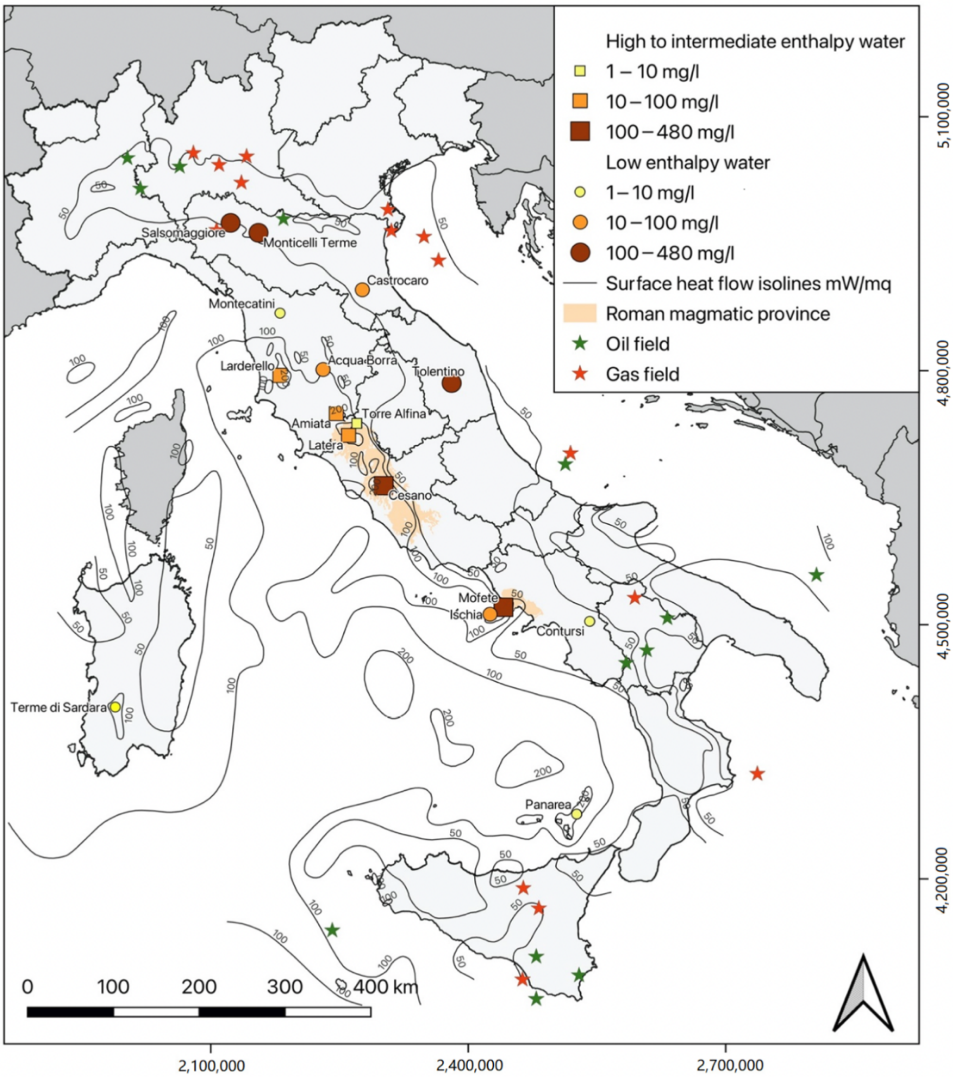

Fig. 14. Lithium-bearing fluids in Italy (Dini et al. 2022). Note that not all known locations with lithium concentrations <10 mg/l are shown here.

4.4.8 Salton Sea (USA)

The US Department of Energy GeoVision study has compiled hydrochemical data from >2'000 wells and hot springs in the USA. It revealed that about 1'200 sites have shown measurable lithium concentrations (Neupane & Wendt 2017). In a subset for the western USA, the study listed 75 sites with measurable lithium content. Of the sites studied, only three geothermal fields (East Mesa, Salton Sea, Wilbur Springs) have lithium concentrations greater than 10 mg/l. The best explored area is the Salton Sea area with 11 operating geothermal power plants and lithium concentrations up to >220 mg/l (Stringfellow & Dobson 2021, Fig. A1). Three companies (Controlled Thermal Resources, Energy Source, Berkshire Hathaway Energy Renewables) are developing chemical processes to extract lithium from geothermal wells making the area to be termed as the "Lithium Valley".

5 Hydrochemical composition of deep fluids in Switzerland

5.1 Introduction

Hydrochemical data from wells in Switzerland are mainly documented in the BDFGeotherm database by Sonney & Vuataz (2007, 2008, Fig. A2) and in several Nagra reports (Waber et al. 2014 and references therein). These two datasets are discussed in the chapters 5.2 (BDFGeotherm) and 5.3 (Nagra).

Good summaries of the geothermal aquifers in Switzerland are given in Nagra (2014) and Waber et al. (2014), with a focus on central northern Switzerland. Previous, very extensive and detailed studies on aquifers in northern Switzerland are documented in the three Nagra reports by Schmassmann et al. (1990), Schmassmann et al. (1992) and Biehler et al. (1993). Chevalier et al. (2010) compiled literature on geothermal aquifers of entire Switzerland and discussed their exploration maturity and summarised their properties (stratigraphic setting, thickness, porosity, permeability, etc.; see Fig. A3 and Fig. A4).

Here we present a compilation and an analysis of the publicly accessible well data that include hydrochemical measurements illustrating the currently known lithium concentrations in deep aquifers in Switzerland.

5.2 BDFGeotherm database

The Swiss Federal Office of Energy (SFOE) mandated the Centre de Recherche en Géothermie (CREGE) in Neuchâtel to compile Switzerland's hydrochemical properties of geothermal fluids in 2007. R. Sonney and F.-D. Vuataz designed the study and R. Sonney completed it as part of his PhD thesis. It resulted in an MS Access database and a descriptive report (Sonney & Vuataz 2007). That database (named BDFGeotherm) contains hydrochemical data from 82 sites with a total of 203 analysed water samples, partly collected at different depths (Fig. A2). 68 of these sites are located in Switzerland and 65 include well data. Some of the measurements do not come from wells but from galleries, tunnels, fountains and springs. These were not used in our compilation.

Measured hydrochemical parameters are the geochemical water type, pH value, temperature, total dissolved solids and the concentrations of Ca, Mg, Na, K, Li, Sr, HCO_3, SO_4, Cl, F and SiO_2 (Fig. 15). It is likely that concentrations of metals/elements, other than lithium, are documented in the original well reports and publications, but were not included in the BDFGeotherm database (R. Sonney pers. comm. 2022).

51 out of 65 well data entries from the BDFGeotherm database contain a lithium concentration measurement (Fig. 16). 45 of which are measured at an aquifer deeper than 100 m. At these 51 well sites, there are 71 water samples in which a lithium concentration was measured (Fig. A5). The spatial distribution of the well sites is very irregular. Most sites are located in the western Valais and in central northern Switzerland. The database includes another 93 analysed water samples from various sites other than wells.

A major shortcoming of the BDFGeotherm database is that the aquifer formation, from which the water samples were collected, is not specified. There is a data attribute "formation", but this is not specific enough to compare those water analyses with other aquifer-specific water analyses from literature. Furthermore, no (analytical) measurement errors are included for the concentrations of cations and anions (dissolved solids) in the fluid samples.

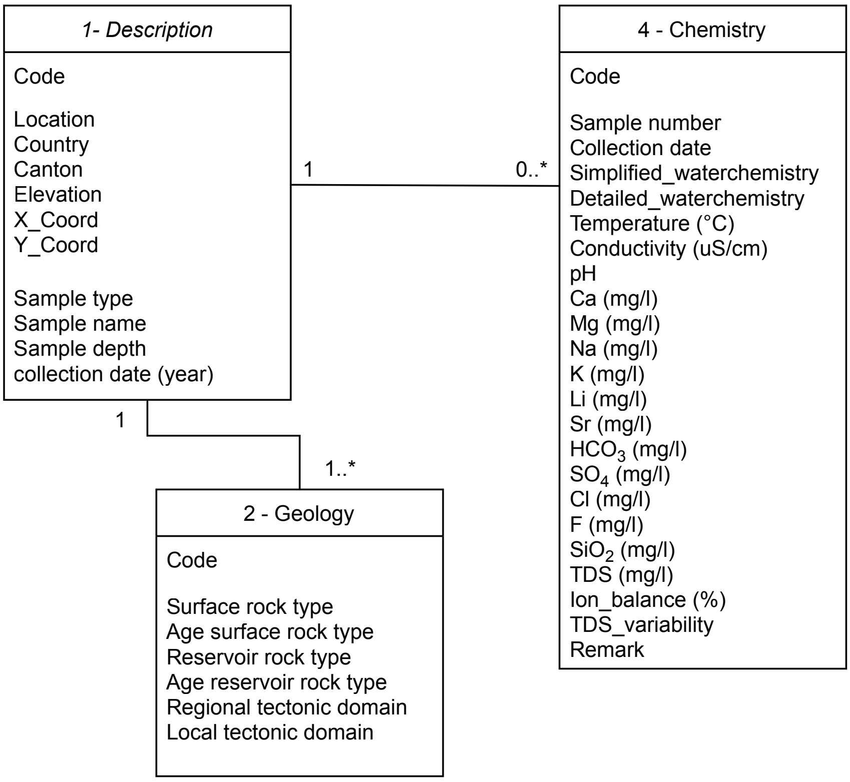

Fig. 15. Overview of the key fields and classes of the BDFGeotherm database.

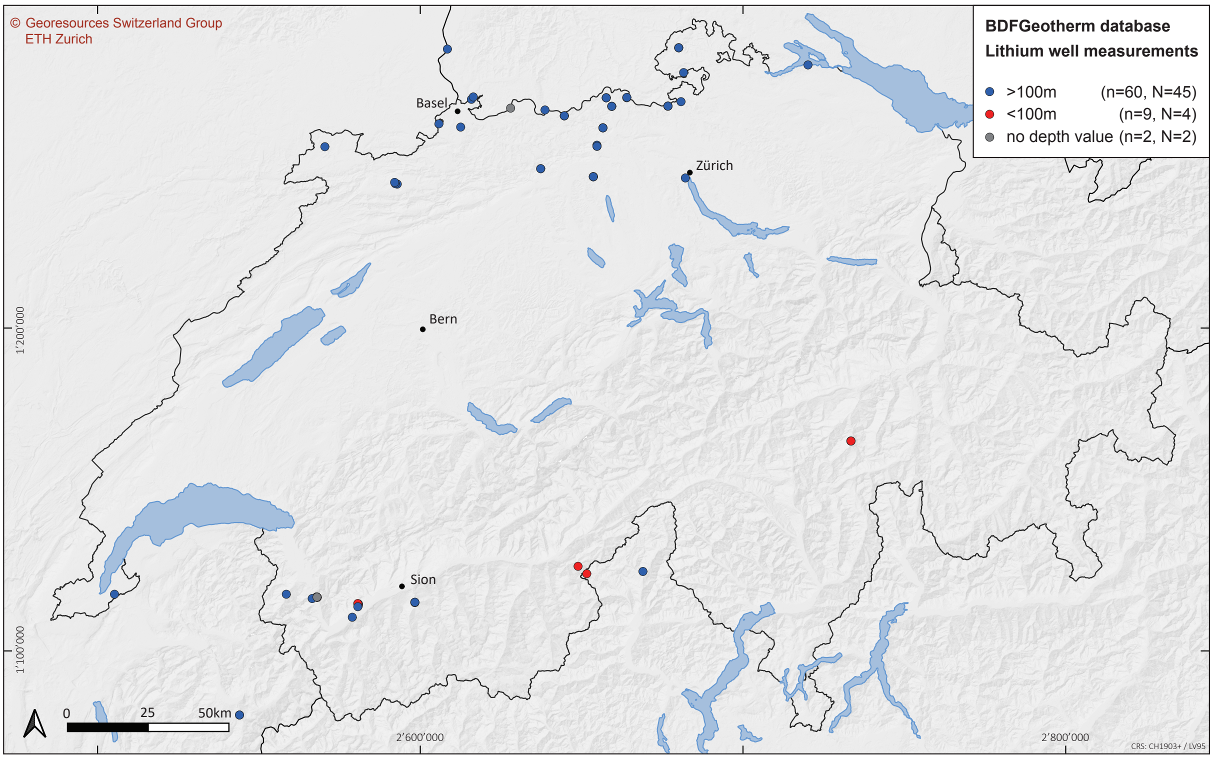

Fig. 16. Compilation of the 51 BDFGeotherm well sites where lithium was measured, separated into wells deeper (blue circles) and shallower (red) than 100 m. N: number of wells, n: number of water samples.

5.3 Nagra dataset

Within the framework of the today completed exploration activities aimed to locate the most suitable location to store radioactive waste (Nagra 2022), Nagra performed a very comprehensive analytical program to study the samples recovered from deep wells, including hydrochemistry. At the time of writing this report, the past and recent hydrochemical analyses are still undergoing a major recompilation (D. Traber pers. comm. 2022). For the present study, Nagra provided us with a consolidated extract of the lithium measurements from the exploration wells in central northern Switzerland compiled before 2019. The recent data collected during the latest exploration phase (2019-2022) could not yet be made available. Note that this Nagra dataset includes well data of non-Nagra origin, such as oil and gas or geothermal exploration wells.

Most of the Nagra data used for our compilation is documented in Nagra (2014) and Waber et al. (2014) and is illustrated in Fig. 17 to Fig. 20. Waber et al. (2014) described more than 2'300 hydrochemical samples obtained from Cenozoic and Mesozoic aquifers (Cenozoic Molasse, Malm limestones, Effinger Schichten, Hauptrogenstein/Birmenstorfer Schichten, Staffelegg Formation, Upper and Middle Keuper carbonates and sandstones, Muschelkalk).

At the moment, we do not have access to the complete Nagra dataset. More data, including measurements of elements/metal other than lithium, are likely to exist and were not included in this study. The dataset that we received does not contain any uncertainty values for the lithium concentrations. According to Waber et al. (2014) and the key references therein, the uncertainties for the lithium values are mostly <5%. For some wells it can be in the order of up to 50% (e.g. Biehler et al. 1993). The recently acquired Nagra well data (e.g. the MAR-1 Marthalen well) show that analytical errors for the lithium concentration measurements are 2-5% (Lorenz et al. 2022). Furthermore, the Nagra dataset used in this study does not contain TDS (total dissolve solids) values (although existing and illustrated in Fig. 18) and does not contain formation temperature for all aquifers. Therefore, it was difficult to compare the Nagra-compiled well data with the BDFGeotherm data.

The Nagra dataset contains 42 wells from which 101 water samples contain a lithium concentration measurement obtained from aquifers deeper than 100 m (Fig. 19 and Fig. 20). Other lithium concentrations were measured at 67 sites: 54 from the surface and 13 values from the Hauenstein tunnel or from an unknown location.

Hydrogeologische Einheit	**Referenz-Datensätze Total**	**Davon mit Vorbehalt (Teildaten)**	**Ober-flächen-nahe GW**	**Tiefe GW**	**Datensätze Untersuchungs perimeter**
Teritär (total)	64	22	32	32	43
Obere Süsswassermolasse (OSM)	22	7	19	3	19
Obere Meeresmolasse (OMM)	20	4	4	16	11
Untere Süsswassermolasse (USM)	22	11	9	13	13
Malm-Aquifer	68	9	36	32	36
Effinger Schichten	4	2	1	3	4
Hauptrogenstein-Aquifer [1)]	12	7	6	6	11
Lias [2)]	10	7	1	9	8
Keuper-Aquifer	39	14	11	28	36
Muschelkalk-Aquifer	91	8	23	70	89

1) Inklusive Birmenstorfer Schichten und einer Probe aus der Wedelsandstein-Formation (Schlattingen-1).

2) Aus Konsistenzgründen mit der älteren Literatur wird hier der Begriff "Lias" anstelle von "Staffelegg-Formation" (Reisdorf et al. 2011) weiterverwendet.

Fig. 17. Aquifers and number of analysed samples per aquifer (column "Referenz-Datensätze Total") of the Nagra study area in central northern Switzerland (Nagra 2014).

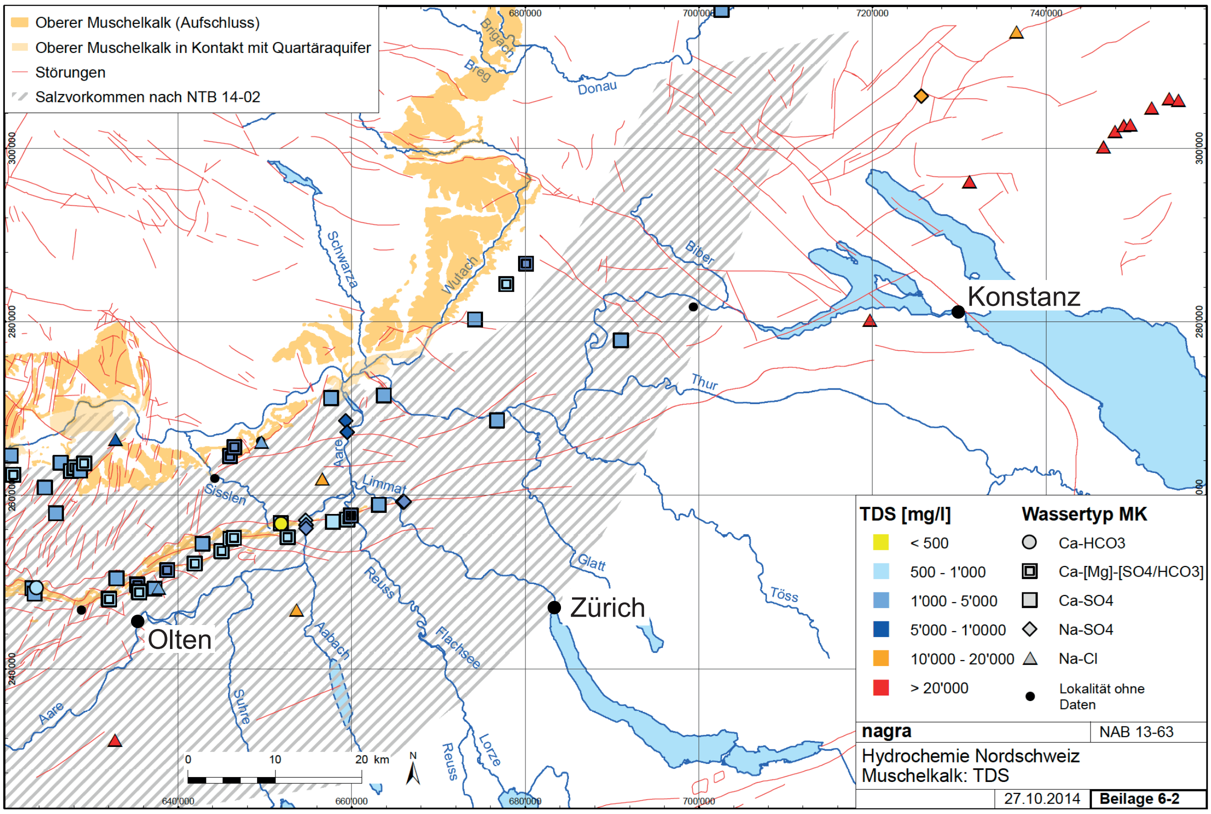

Fig. 18. Total dissolved solids (TDS) and water types from the Upper Muschelkalk formation (modified from Waber et al. 2014). Orange polygons: exposures of the Upper Muschelkalk Formation. Dashed area: occurrence of Triassic salt in the subsurface. The two red triangles in Switzerland show the high salinity (TDS >20'000 mg/l) water samples from the Pfaffnau and Berlingen wells. Northeast of the Lake Constance, high salinities are observed in the Upper Muschelkalk. See the lithium concentrations of these wells in Fig. 24.

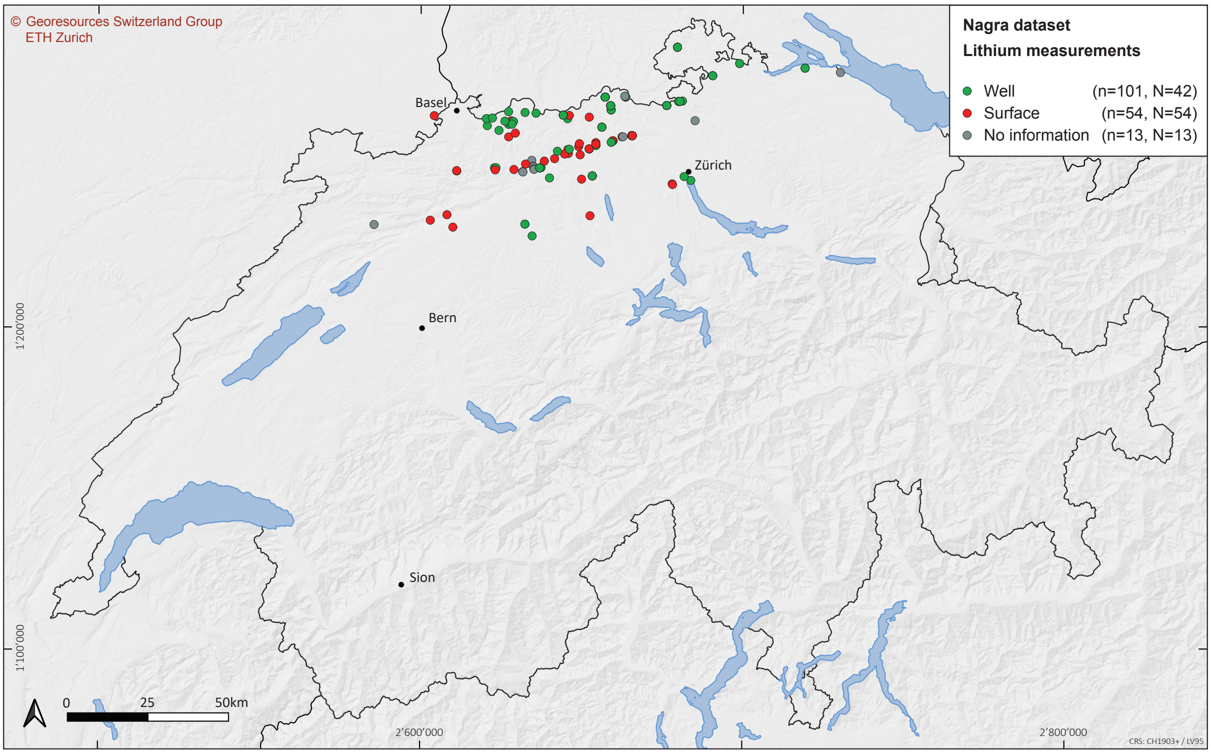

Fig. 19. Compilation of well sites and surface locations with lithium measurements from the Nagra dataset (N: number of wells, n: number of lithium measurements). The 13 grey circles show wells that have no information about the water sample type, nine of them are from the Hauenstein base tunnel.

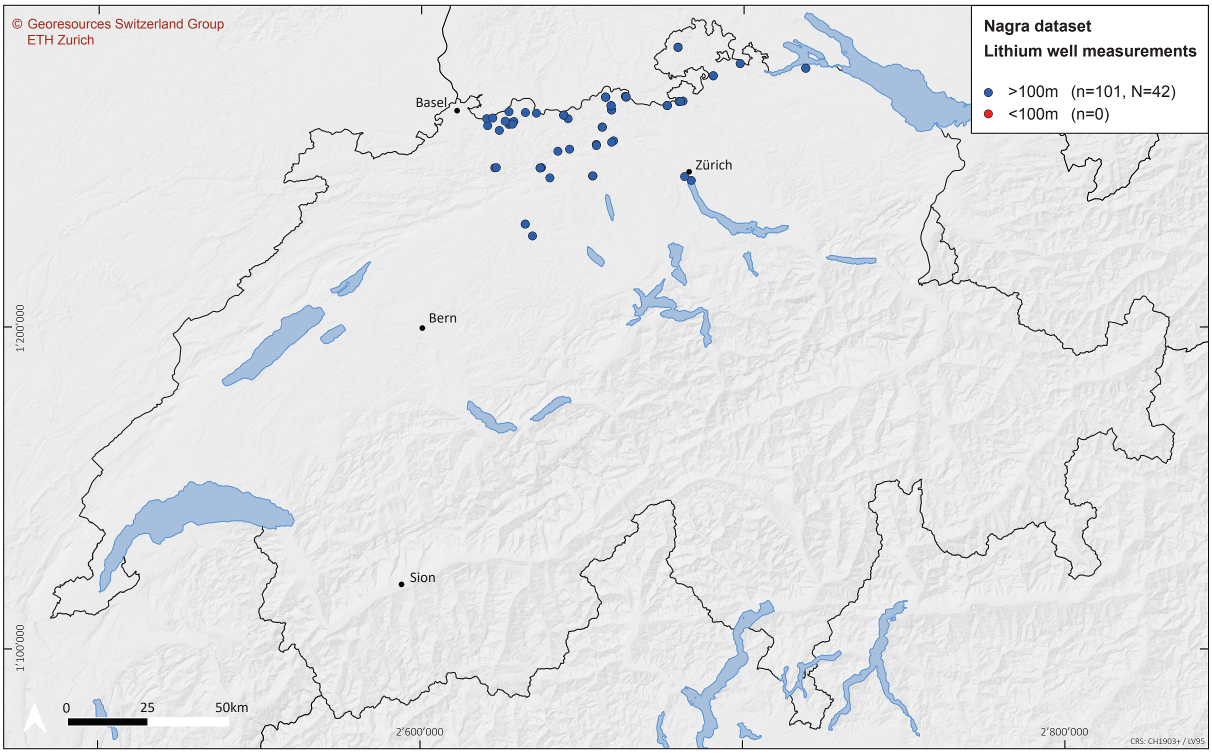

Fig. 20. Compilation of well sites with lithium measurements from the Nagra dataset (N: number of wells, n: number of lithium measurements). Note that all these samples are from wells deeper than 100 m.

5.4 Swisstopo database

The Swiss Geological Survey at swisstopo hosts a well database published on the Federal Geodata Viewer map.geo.admin.ch (layer "Wells >500 m") that contains 182 wells (status of the published layer as of 30.10.2018). 27 of these wells are open access, 155 are restricted. Given the limited data access, it was not possible to verify whether the corresponding well reports contain hydrochemical data usable for our compilation. However, 30 of these 155 wells showed up in either the Nagra or the BDFGeotherm databases. 15 of these 30 wells contain a lithium measurement, and are part of our compilation figures. From the 27 open access wells, there are 13 contained in either the Nagra-derived or the BDFGeotherm database and 10 of them have a lithium measurement.

One of the best studied, more recent well is the Basel-1 well. In the swisstopo database, the well is treated as restricted. However, analyses of hydrochemical data from that well are published in various articles (e.g. Ladner et al. 2008, Stober et al. 2022b). The thermal water was not analysed at depth but at the outflow on the surface. There, total dissolved solids (TDS) were around 16'000 mg/l and lithium concentrations of ca. 30 mg/l were measured. Stober et al. (2022b) concluded that this NaCl-type water has a typical hydrochemical composition of a deep water from the crystalline basement (about half of the ca. 5 km deep borehole penetrated the crystalline granitic basement).

5.5 Compilation approach

For our evaluation, we combined the BDFGeotherm database with the dataset we received from Nagra. We built our compiled database essentially on two tables (Fig. 21). Table "well" manages core information regarding each well site, mainly including XYZ coordinates, depth and name. Table "Hydro_measurements" contains all information about each hydrochemical measurement including meta information such as sample depth, sampling date as well as hydrogeological formation at the sample location. This structure is specifically designed to combine the two original datasets (BDFGeotherm, Nagra). However, there are only a few measurements for which all attributes are available. For example, from Nagra, we received only the lithium concentrations, but not other elements or metals and no TDS numbers. From the BDFGeotherm database we have no detailed information on the aquifer formations.

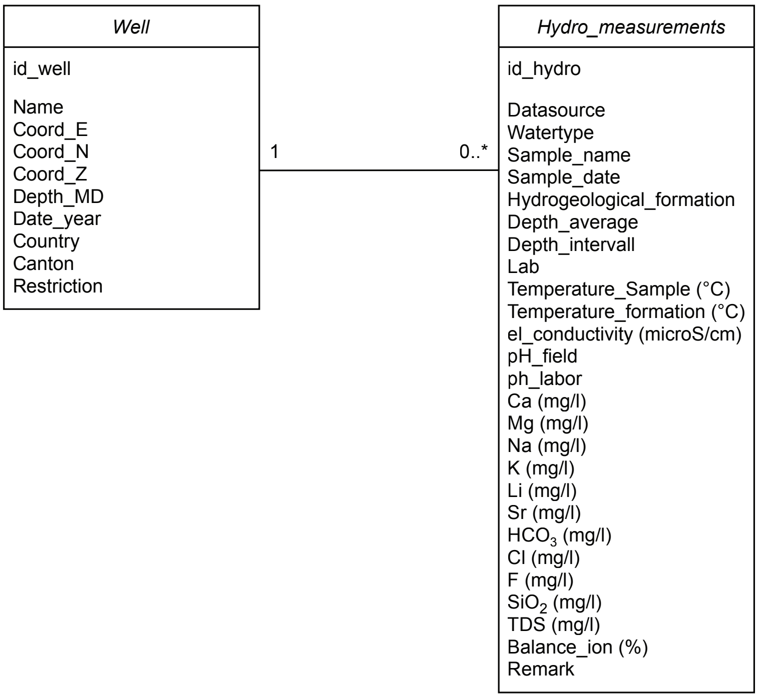

Fig. 21. Data structure and attributes of the compiled database in this project.

Focusing on wells deeper than 100 m, we combined the 51 wells with a lithium measurement from the BDFgeotherm database (Fig. 16) with the 42 wells with a lithium measurement from the Nagra dataset (Fig. 20). The result of this combination is illustrated in Fig. A6. These wells are concentrated in central northern Switzerland and in the Valais. Note that 12 wells (with 23 lithium measurements) are duplicates. The BDFGeotherm database does not contain 28 wells that were drilled before 2007 and compiled by Nagra (Fig. A7).

Our compilation results in a final lithium concentrations dataset of 79 wells with 149 lithium measurements.

In a last step, we added the locations of the 182 additional wells from the swisstopo well database (map.geo.admin.ch, layer "Wells >500 m") to our compilation, pointing out that potentially more (hydrochemical) well data might be available (Fig. 22). After removal of duplicates (swisstopo wells with lithium measurements already part of our BDFGeotherm-Nagra compilation), our database compiled in this study contains additional 157 swisstopo wells that potentially have a lithium concentration measured.

5.6 Summary and discussion of today available hydrochemical data from wells in Switzerland

Our compilation shows that average lithium concentrations in Swiss wells range between 1 to 16 mg/l, depending on the aquifer formation (Tab. 3). We identified two wells (Pfaffnau, Berlingen) with above-average lithium concentrations (82 mg/l in Pfaffnau, 144 mg/l in Berlingen, Fig. 23) at the level of the Upper Muschelkalk aquifer in the Swiss Molasse Basin (Heuberger et al. 2022). However, Waber et al. (2014) stated that there is too little data from those hydrocarbon wells about the fluid sampling and testing procedures to make a reliable quantitative statement. Therefore, given the significant uncertainty associated with this data, these lithium concentrations should be treated with caution. Although uncertainty (i.e. analytical error) estimations are specified in the Nagra reports (Waber et al. 2014 and references therein), the Nagra dataset does not contain any uncertainty values for the measured lithium concentrations. Apart from the two above wells, the remaining ones have lithium concentrations of less than 33 mg/l at various aquifer formations (Fig. 23). Lithium-bearing aquifer formations are mainly the Permo-Carboniferous, the crystalline basement or the Upper Muschelkalk (Fig. 24, Tab. 3), with just one well (Berlingen), where elevated lithium concentrations were measured in the Upper Jurassic (Malm) aquifer. The most saline fluids of the Swiss Molasse Basin (TDS values up to 120 g/l) are located in sedimentary aquifers (Permo-Carboniferous or Buntsandstein aquifers) with reservoir temperatures below 70 °C (Waber et al. 2014, Sanjuan et al. 2016).

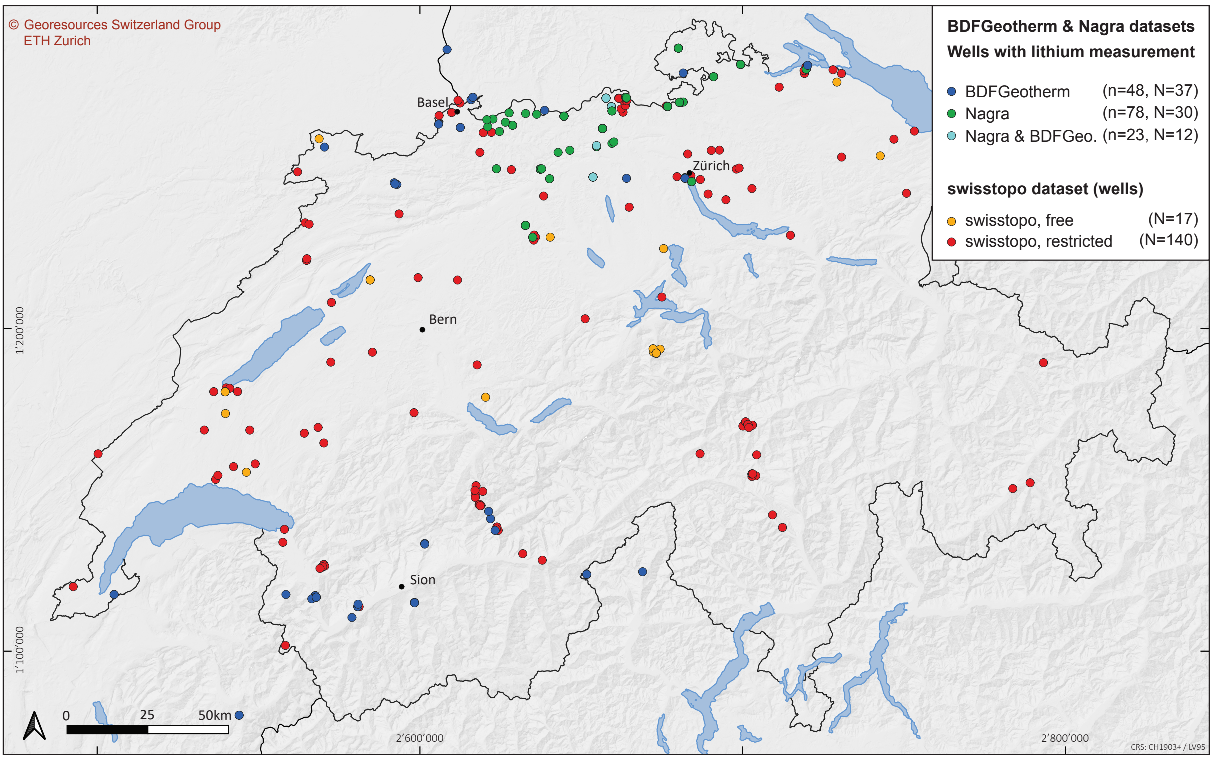

Fig. 22. Compilation of the 79 well sites with lithium measurements (see also Fig. A6) in combination with the swisstopo wells deeper than 500 m (map.geo.admin.ch). Note that for most of the swisstopo wells it is not documented whether they contain a lithium measurement. There are 10 free and 15 restricted swisstopo wells shown with lithium measurements that have a Nagra or BDFGeotherm affiliation (i.e. double entries). N= number of wells >100 m (>500 m in case of the swisstopo wells), n= number of lithium measurements.

Compared to the wells in the Upper Rhine Graben, the lithium concentrations as well as the TDS and the geothermal gradient are significantly lower in Switzerland (Fig. 24). It would be very interesting to compare the well data from the Swiss Molasse Basin with the data, along strike, just northeast of Lake Constance in the southwesternost German Molasse Basin. Stober (2014) reported lithium concentrations of 140-165 mg/l from the Upper Muschelkalk aquifer at four of those wells, of which the well names are not specified. Therefore, well locations could only be tentatively assigned in our Fig. 24. It should be reviewed whether there is a genetic link between the high salinity and lithium enriched Muschelkalk aquifers in the SW German Molasse Basin and the stratigraphically related aquifers along strike further southwest in the Swiss Molasse Basin.

Sanjuan et al. (2016) compared different aquifer types and geological provinces in Europe in the framework of the EuGeLi project (chapt. 4.3.4). They concluded that compared to the Upper Rhine Graben (Na-Cl waters with TDS of ca. 100-200 g/l and 115-200 °C at reservoir depth), the salinity of fluids in the adjacent northern Swiss Molasse Basin is significantly lower (generally TDS <2 g/l, with some exceptions of up to 16 g/l) and temperatures at depth are lower (25-110 °C at the depth of the crystalline or Permo-Carboniferous basement). Based on isotope proxies of the crystalline basement rocks, they proposed a different lithium origin in the Swiss wells (i.e. other than from fluids circulating in the crystalline basement of the Upper Rhine Graben). Waber et al. (2014) interpreted that the chemical composition and the available isotopic data from the Muschelkalk fluids could locally (Basel and Baden regions) point to an origin from the basement (crystalline and/or Permian) and/or from the lowermost

Mesozoic Buntsandstein aquifer. However, due to the absence of detailed and comparable data, this relationship remains to be demonstrated (Waber et al. 2014).

Since the BDFGeotherm database also contains water analyses from tunnels, we additionally looked at some of these with lithium measurements for comparison: in the Simplon and Loetschberg railway tunnels the lithium concentrations range between 0.02 and 3.05 mg/l (Sonney & Vuataz 2007). More recent studies have shown that lithium concentrations from water samples in the new Gotthard railway base tunnel reach up to 4 mg/l, and that the total dissolved solids (TDS) range between 115 and 3’675 mg/l, with the typical basement fluids of the Gotthard nappe having TDS of 250 mg/l or lower (Bucher et al. 2012, Stober et al. 2022a).

Tab. 3. Descriptive statistics on the lithium concentration of water samples (n) from wells deeper than 100 m in Switzerland. This table does not show all available lithium measurements because the BDFGeotherm database, containing 45 wells with a lithium measurement, does not specify aquifer formations (compare with Fig. 16 and Fig. A6).

Tectonic area	**Aquifer Formation**	**Era**	**n**	**max.** [mg/l]	**median** [mg/l]	**average** [mg/l]
Molasse Basin & Jura	OMM (Miocene)	Cenozoic	2	0.11	0.07	0.07
Molasse Basin & Jura	USM (Oligocene-Miocene)	Cenozoic	6	1.9	0.6	0.8
Molasse Basin & Jura	Upper Jurassic (Malm)	Mesozoic	2	1.2		1.0
Molasse Basin & Jura	Lower Jurassic (Liassic)	Mesozoic	1	12	12.0	12.0
Molasse Basin & Jura	Upper Muschelkalk	Mesozoic	35	144	0.1	7.0
Molasse Basin & Jura	Keuper	Mesozoic	5	28	1.8	9.4
Molasse Basin & Jura	Buntsandstein	Mesozoic	11	14.4	4.0	4.7
Molasse Basin & Jura	Permian	Paleozoic	6	32.3	15.5	15.7
Molasse Basin & Jura	Crystalline Basement		32	14.5	1.4	2.3
Alps & Southalpine	*various*	*various*	24	3.7	0.4	0.8

As the currently available datasets (BDFGeotherm & Nagra compilations) are not complete, parameters like TDS, formation temperature, aquifer formation were not available to us for all the wells. Thus, it was not possible to derive correlation relationships between for example lithium concentration and TDS or formation temperature. However, from the available data we can conclude that water samples in Switzerland with lithium concentrations >10 mg/l are all Na-Cl water types. This is also true for lithium-rich geothermal fluids in Europe (Italy, Germany, France) where these fluids have TDS >56’000 mg/l and temperatures of >120 °C (Sanjuan et al. 2022). Thus, high TDS and temperature values seem to be key factors for high lithium concentrations in deeps fluids. This is nicely illustrated in the Upper Rhine Graben, where lithium-rich geothermal brines are all located in areas with very high heat flow (Fig. 25). However, Sanjuan et al. (2022) have shown that these two factors alone are not sufficient to explain that apparent correlation. High lithium concentrations also depend on the type of reservoir rock and its mineralogical constituents. When comparing the lithium concentrations in Switzerland (Fig. 24) with the heat flow (Fig. 26), it seems that the enrichment of lithium in geothermal fluids correlates with high heat flow. However, note that the heat flow map of Switzerland is based on comparably few (108 wells), unevenly distributed wells (Medici & Rybach 1995).

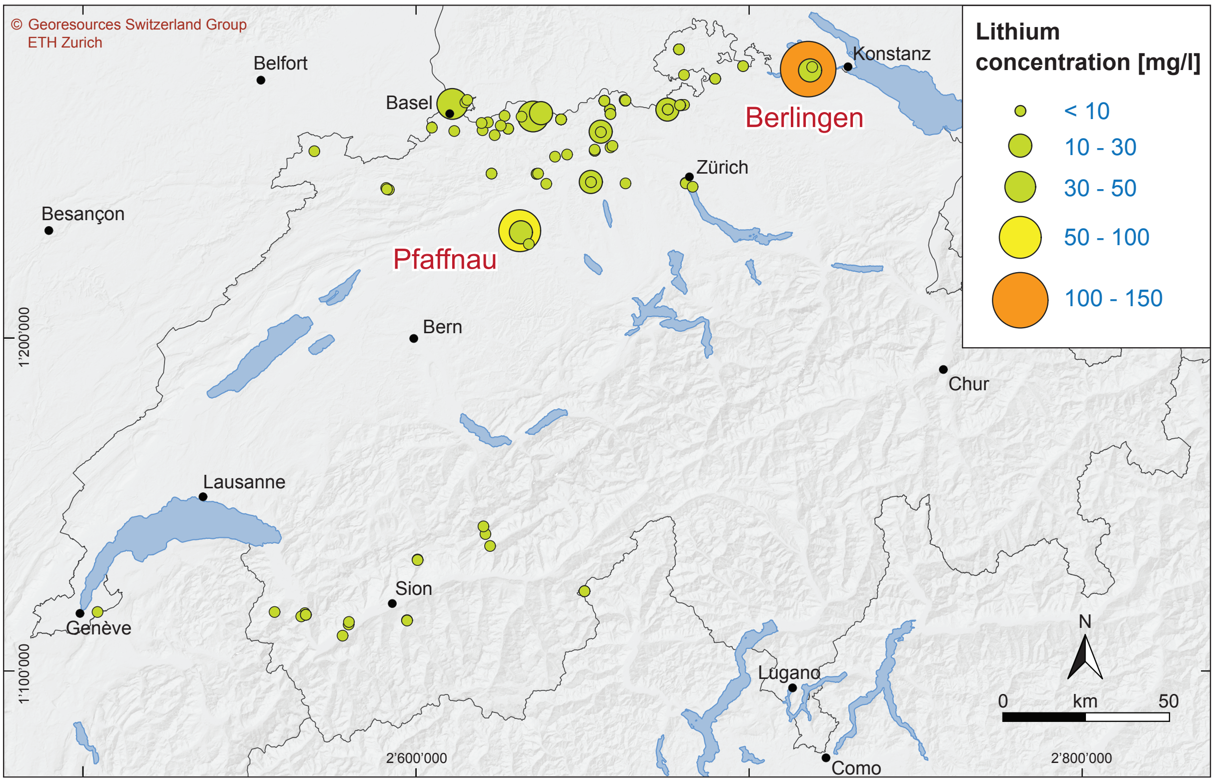

Fig. 23. The 79 well sites with lithium measurements in Switzerland, grouped by the lithium concentration. Note the elevated concentrations at Pfaffnau (82 mg/l) and Berlingen (144 mg/l).

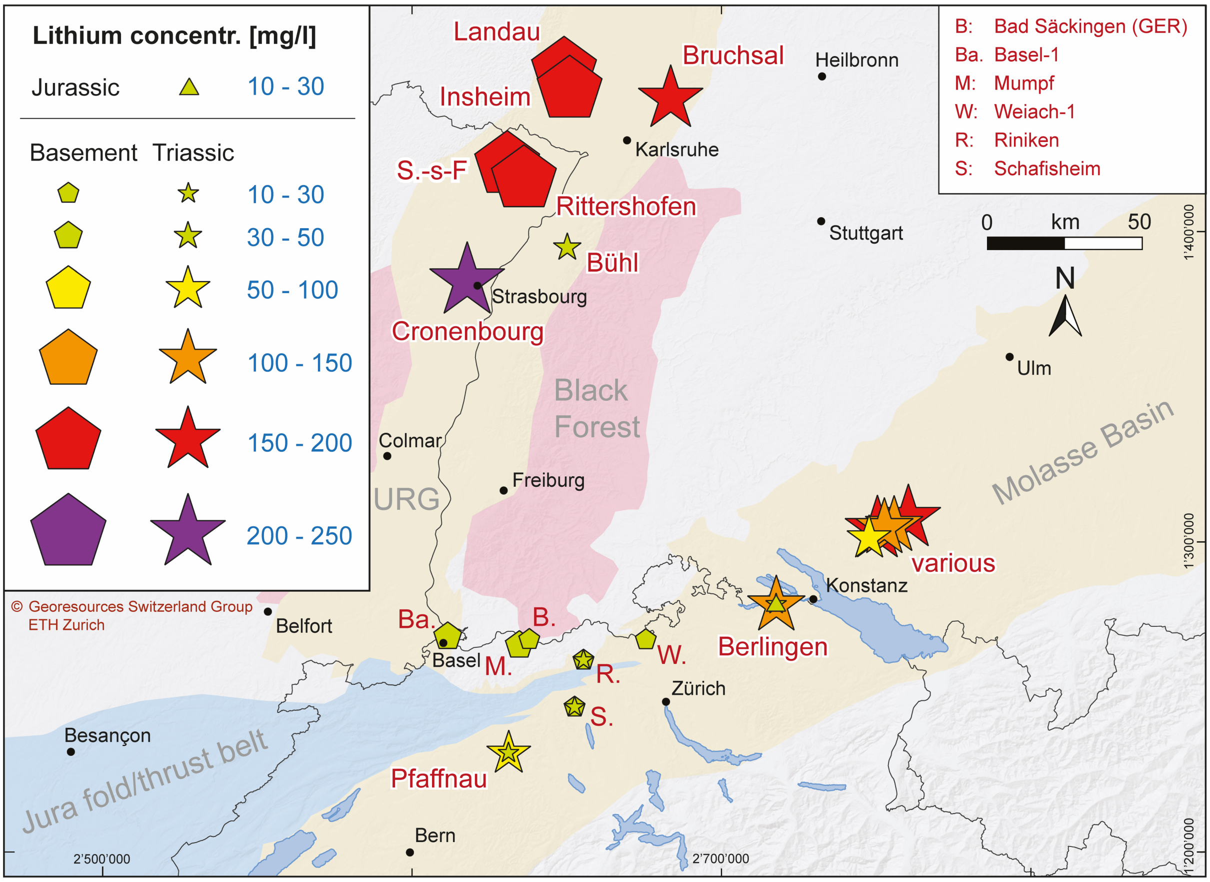

Fig. 24. Lithium concentrations in Swiss wells compared to the ones in the Upper Rhine Graben (URG) and the southwesternmost German Molasse Basin, with well symbols according to the geothermal aquifer formation. Only lithium concentrations >10 mg/l are shown. See text for more details.

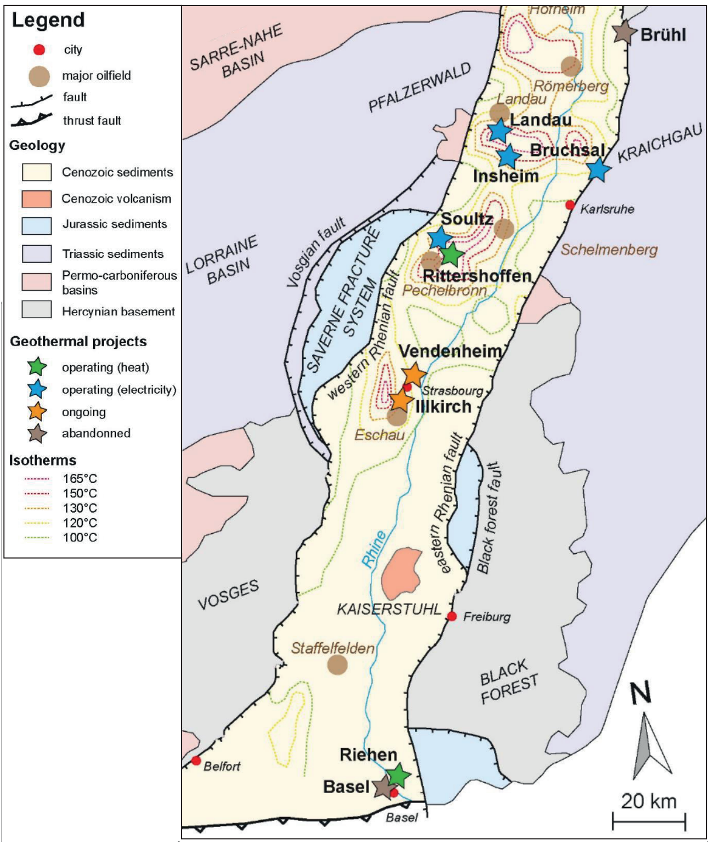

Fig. 25. Geothermal wells and temperature isotherms at 2 km depth in the Upper Rhine Graben (extracted from Glaas 2021). See Fig. 24 for the lithium concentrations in the geothermal wells. Note that geothermal fluids with lithium concentrations >150 mg/l are all located in areas with high heat flow (isotherms >120 °C).

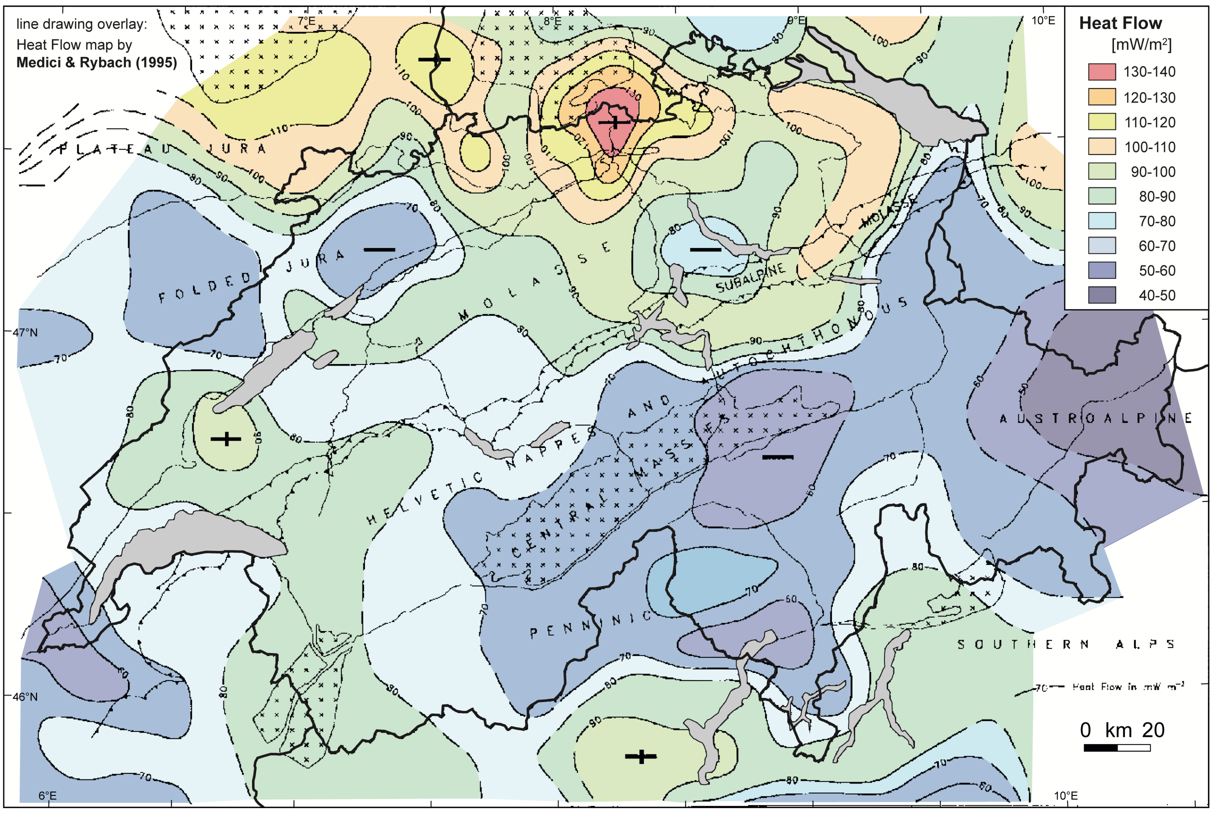

Fig. 26. Heat flow map of Switzerland, modified (i.e. coloured and annotated) from Medici & Rybach (1995). Note that this map is based on well data evaluated in the early 1990s and therefore does not take into account more recent well and tunnel temperature data.

6 Conclusions

This literature review and compilation of well data gives an overview of the technical and geological background of lithium extraction from geothermal fluids in Western Europe and on the lithium occurrences in the Swiss deep fluids known today.

Chapter 3 summarises the chemical and mineralogical situation of lithium compounds, their natural occurrence and the technical application of this metal in the framework of the energy transition.

Chapter 4 documents the most relevant ongoing and planned lithium exploration and extraction projects, mainly located in Western Europe and with a focus on the Upper Rhine Graben. Since these national and international research and industry projects evolve quickly, we provided website links in the corresponding subchapters for accessing the most up-to-date information.

Chapter 4 describes the concentrations of lithium in geothermal brines in Switzerland based on publicly accessible data from wells deeper than 100 m.

Our analysis shows that:

- There are 79 wells with publicly accessible lithium measurements that are concentrated in central northern Switzerland and in the Valais (Fig. 23). In the rest of Switzerland, there are no freely accessible hydrochemical data from wells (Fig. A6).
- For most of the wells, we only had access to lithium measurements. For 95% of the data, the lithium concentrations range between 0.4 and 15 mg/l. Our results highlight that lithium occurs in the Muschelkalk and Permian aquifers, but also in the Oligocene-Miocene, Upper Jurassic, Liassic, Keuper, Bundsandstein and crystalline basement aquifers (Tab. 3). We did not have error estimates available for the lithium concentrations. However, literature data show that (analytical) uncertainties are usually in the order of 2-5% but can be up to 50%. Generally, our dataset is heterogeneous in terms of available information on sample quality and analytical methods, partly because the data have been acquired over several decades. Therefore, caution is required in the interpretation.
- We identified two wells (Pfaffnau, Berlingen) with elevated lithium concentrations (82 and 144 mg/l, respectively) in the Muschelkalk aquifer. Those two wells are hydrocarbon exploration wells drilled in 1963 and 1964. These comparatively high lithium concentrations should be considered with caution before making further interpretations (Waber et al. 2014). If the wells are still accessible, it would be reasonable to resample and reanalyse the fluids to confirm the previous measurements.
- The lithium concentrations in Switzerland (<150 mg/l) are lower than those from the nearby Upper Rhine Graben (150-250 mg/l). However, there are certain geological areas in Switzerland (Fig. 24) with geothermal fluids that have elevated total dissolved solids (TDS) values and lithium concentrations >30 mg/l. With the currently available data, the Molasse Basin in the area of Lake Constance as well as the Basel and Lower Aare Valley areas appear most promising to conduct further investigations.
- The analysed data indicate a correlation between high TDS values and areas of high local heat flow. This correlation is well established in the Upper Rhine Graben (Fig. 25), in Italy (Fig. 14) and somewhat indicated in central northern Switzerland (Fig. 24, Fig. 26). It is less clear in the Lake Constance area. However, for a more precise conclusion, more temperature data from deep wells are needed. Today, deep wells in Switzerland are rather sparse and unevenly distributed. Up-to-date heat flow maps could be useful as indicator for the exploration of metal-rich geothermal brines.
- The process of lithium enrichment in geothermal fluids at depth is not yet sufficiently understood and requires more research.
- With the today available knowledge in Switzerland, it is not possible to define a cut-off value for lithium concentrations from geothermal fluids as an economic parameter. This would only be possible with integrated geothermal reservoir analyses at local/regional scale, long-term monitoring

of geothermal fluid flow rates and metal concentrations in the fluids, combined with an analysis of the current and future market development.

Today, less than half of the data from the deep wells in Switzerland are freely accessible. Our study shows that there are not enough wells with hydrochemical measurements for most areas of Switzerland to establish a fact-based understanding of the deeper underground regarding the regional occurrence, distribution and source of lithium or other critical raw materials. A lot of potentially useful information could be contained in the 155 wells that are currently classified as restricted. Only free access to this data can enable a robust characterisation of the Swiss subsurface. As shown with the motion by M. S. Jauslin (2020) on exploration of the Swiss subsurface in the Swiss parliament or with the recent interpellation by M.-O. Buffat (2022) on potential lithium occurrences in the Canton de Vaud, there is an obvious requirement to better characterise the geological underground to address future societal and environmental challenges in Switzerland.

7 Recommendations

Based on our investigation and aiming at establishing a Switzerland-wide database of critical raw materials (i.e. lithium) potentially occurring in deep aquifers, we recommend the following measures:

- Nagra is still evaluating and documenting their results of the 2019-2022 drilling campaign. Technical and publicly accessible reports will be available not earlier than by the end of 2023 (D. Traber pers. comm. 2022). As soon as available, these data should be used to resume and extend our present investigation. This appears valuable although these wells are located "only" in the Nagra investigation area in central northern Switzerland and thus in an area with already comparatively many well data. Preliminary results of that drilling campaign indicate low lithium concentrations in the range of 0.1-2.1 mg/l in the Upper Jurassic, Keuper and Muschelkalk aquifers (D. Traber pers. comm. 2022).
- Swisstopo and SFOE should obtain formal agreements with the owners of the restricted wells to make use of the relevant hydrochemical data contained therein.
- The well data northeast of Lake Constance in the southwestern German Molasse Basin, where lithium concentrations reach up to 162 mg/l, should be obtained and reviewed. It should be tested whether there is a genetic link between the high TDS and high lithium Muschelkalk aquifers and the stratigraphically related aquifers along strike further southwest in the Swiss Molasse Basin, for example at the Berlingen or even the Pfaffnau well sites (Fig. 18, Fig. 24).
- As swisstopo is in the process of consolidating and harmonising its well database, it is worth waiting for this repository to be completed before a more sophisticated hydrochemical well database will be established at a national scale. With this updated swisstopo well database, the well database compiled in this study could be further harmonised and extended. Missing attributes or values, if available, should be added (i.e. to wells mainly derived from the BDFGeotherm database). Such attributes are the aquifer formation, the aquifer or sample depth, the flow rate, and, most importantly, the concentration of lithium and other critical raw materials.
- The lithium concentrations compiled in this study are mainly derived from hydrocarbon exploration wells. Therefore, the hydrochemical analyses likely were not focusing on accessory minerals/ metals like lithium. In the case of a comprehensive exploration program, we recommend the well data to be further reviewed by hydrogeology/hydrochemistry experts and, if still accessible, to resample and reanalyse fluids from certain wells.
- Several European ongoing projects are compiling well data with focus on critical metals like lithium, at a European or national scale. These are (1) the Reflect project (chapt. 4.2.1), (2) the CRM geothermal project (chapt. 4.2.2), (3) the Li+Fluids project (chapt. 4.3.3) and (4) the BrineMine project (chapt. 4.4.3). A data and know-how exchange with the institutions running these analyses should be established.
- For better understanding the origin of critical raw materials like lithium in saline aquifers in Switzerland, and to guide future exploration activities, we recommend to further analyse the geological setting (stratigraphy, rock/aquifer properties, local/regional heat flow, tectonic setting, etc.) in order to characterise the potential metal-bearing aquifers (reservoir volumes, flow rates, water chemistry, critical raw material content, compare Fig. A3, Fig. A4).
- Finally, we recommend the establishment of a sampling and testing protocol to the permitting authorities at Canton level to force the operators of the federally-subsidised geothermal projects to perform a comprehensive hydrochemical analysis of the deep fluids encountered during the drilling progress of the geothermal wells. Swisstopo, SFOE and our group are already working on that and are in contact with experts from Germany and France to collect know-how for such sampling procedures for deep fluids and corresponding analytical evaluations.

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9 Data repository

The data compiled in this study is stored at the Swiss Geological Survey (swisstopo) and is available on request from infogeol@swisstopo.ch.

10 Appendix

Tab. A1. Major hard-rock lithium minerals with their average Li_2O content (Bowell et al. 2020)

Mineral	Formula	Li_2O, wt%	Comment
Spodumene	$LiAlSi_2O_6$	6–9	Major ore
Petalite	$LiAlSi_4O_{10}$	4.73	Common in African ores
Lepidolite (series polylithionite–trilithionite)	$KLi_2Al(Si_4O_{10})(F,OH)_2$ to $K(Li_{1.5}Al_{1.5})(AlSi_3O_{10})(F,OH)_2$	4.19	Widespread in low-grade ores especially Australia
Zinnwaldite (series siderophyllite–polylithionite)	$KFe^{2+}{}_2Al(Al_2Si_2O_{10})(OH)_2$ to $KLi_2Al(Si_4O_{10})(F,OH)_2$	2–5	Common in European greisen ores
Amblygonite	$Li,Al(F,OH)PO_4$	7.4	Common in African ores e.g., Zimbabwe
Montebrasite	$LiAl(PO_4)(OH)$	7.4	Common in African ores
Eucryptite	$LiAlSiO_4$	9.7	Common in African ores
Triphylite	$Li(Fe,Mn)PO_4$	9.47	Common in African ores
Jadarite	$LiNaSiB_3O_7(OH)$	7.3	Only present at Jadar (Serbia)
Hectorite	$Na_{0.3}(Mg,Li)_3(Si_4O_{10})(F,OH)_2{\cdot}nH_2O$	<1–3	Main ore in volcanic tuff hosted ores

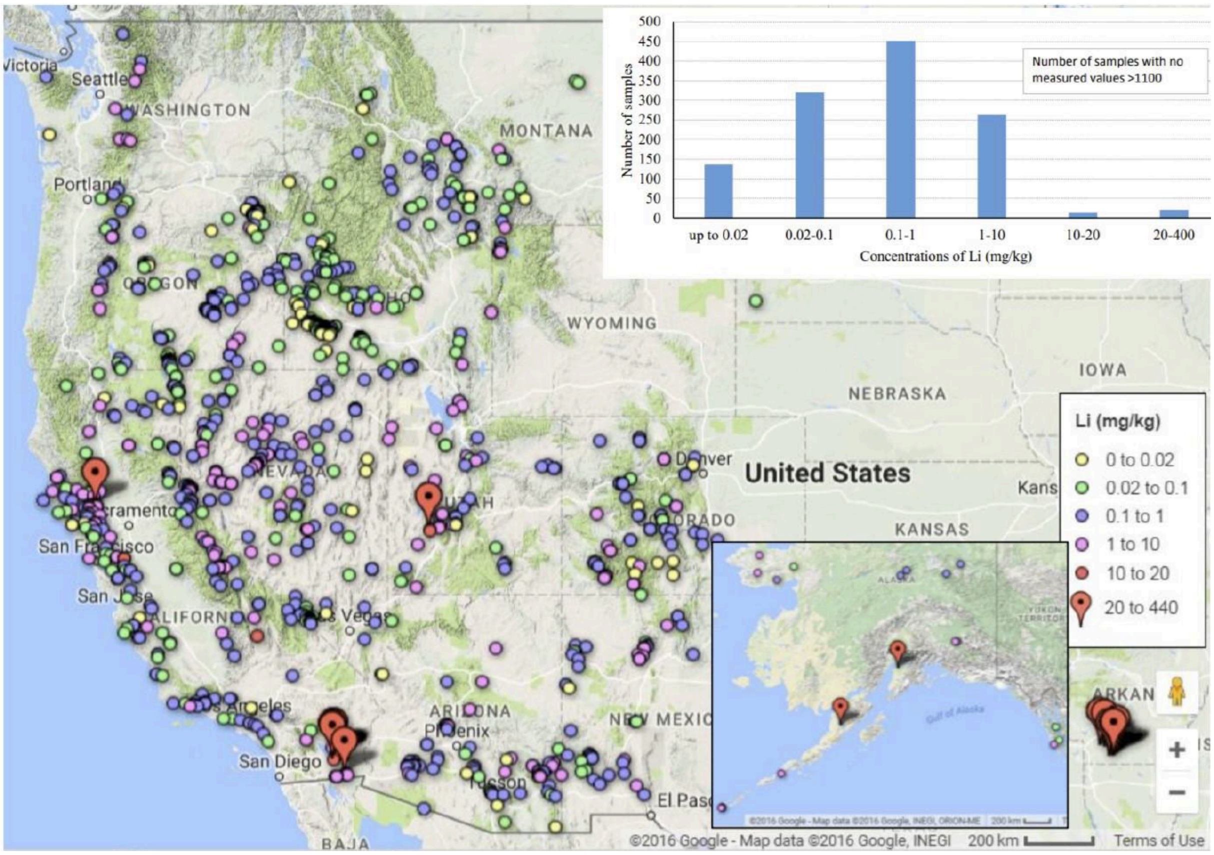

Fig. A1. Distribution of geothermal brine samples in the USA with measured lithium concentrations (Stringfellow & Dobson 2021). Note that among those many well sites less than 5% have lithium concentrations >20 mg/l.

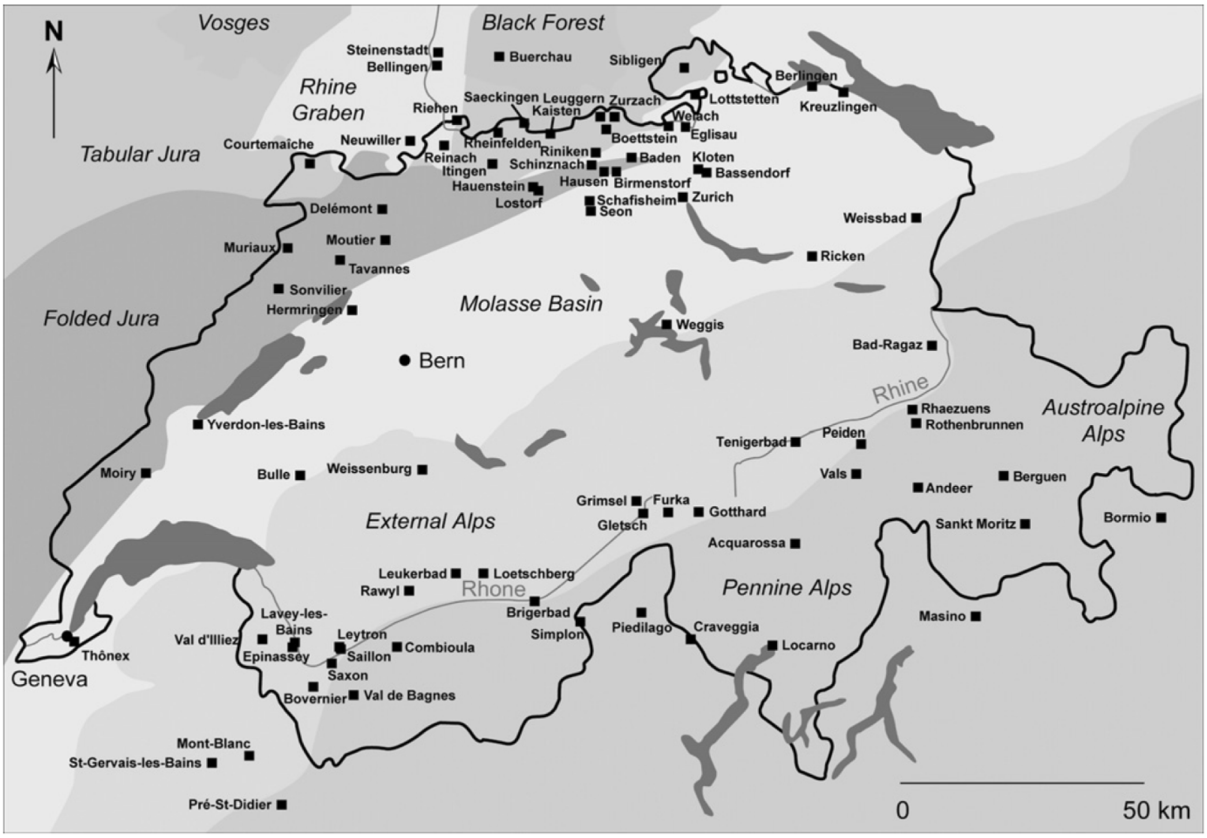

Fig. A2. Locations of geothermal sites (wells, tunnels, springs) in the BDFGeotherm database (Sonney & Vuataz 2008).

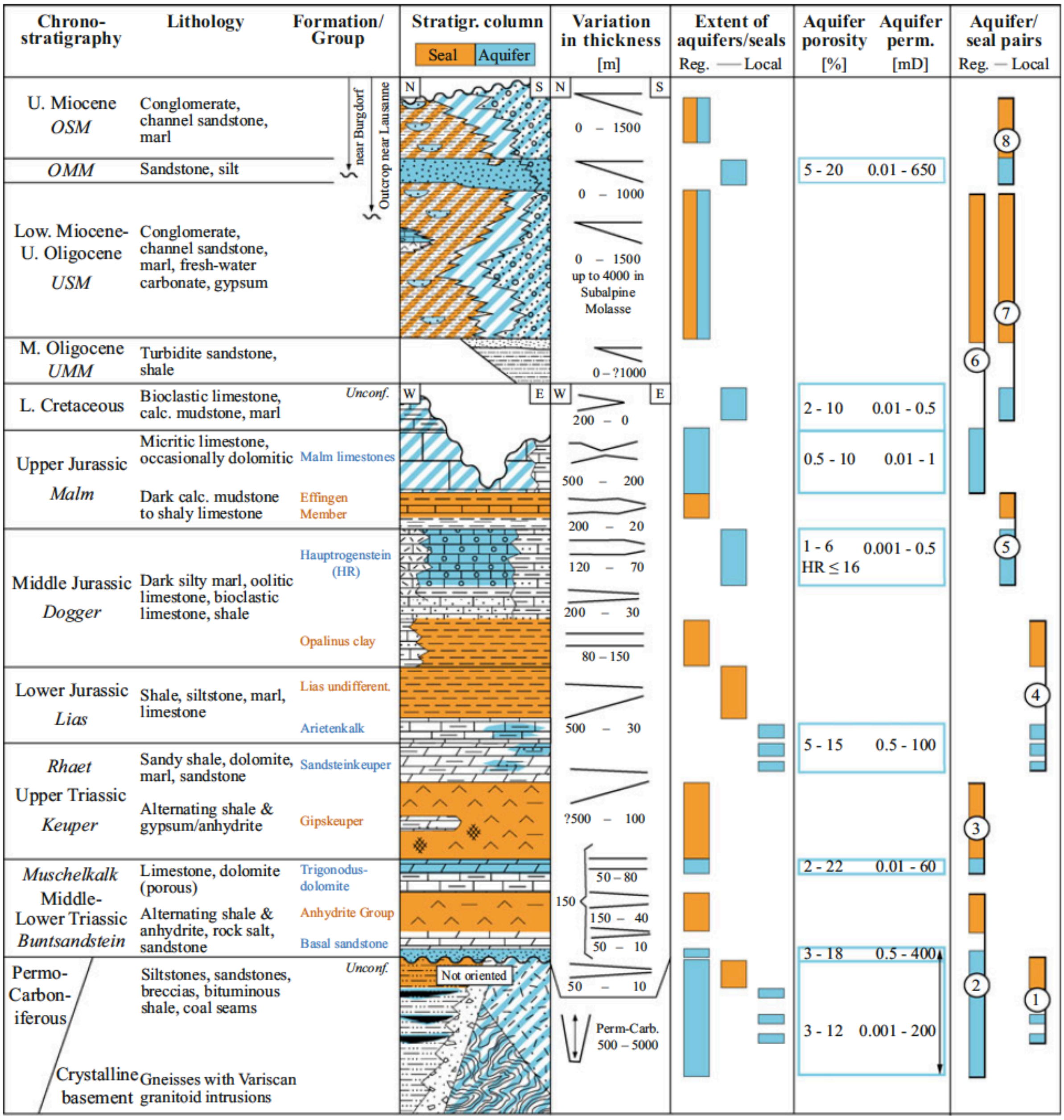

Fig. A3. Generalised stratigraphic column (not to scale) of the Swiss Molasse Basin and the adjacent Jura fold-and-thrust belt with key aquifer properties (Chevalier et al. 2010).

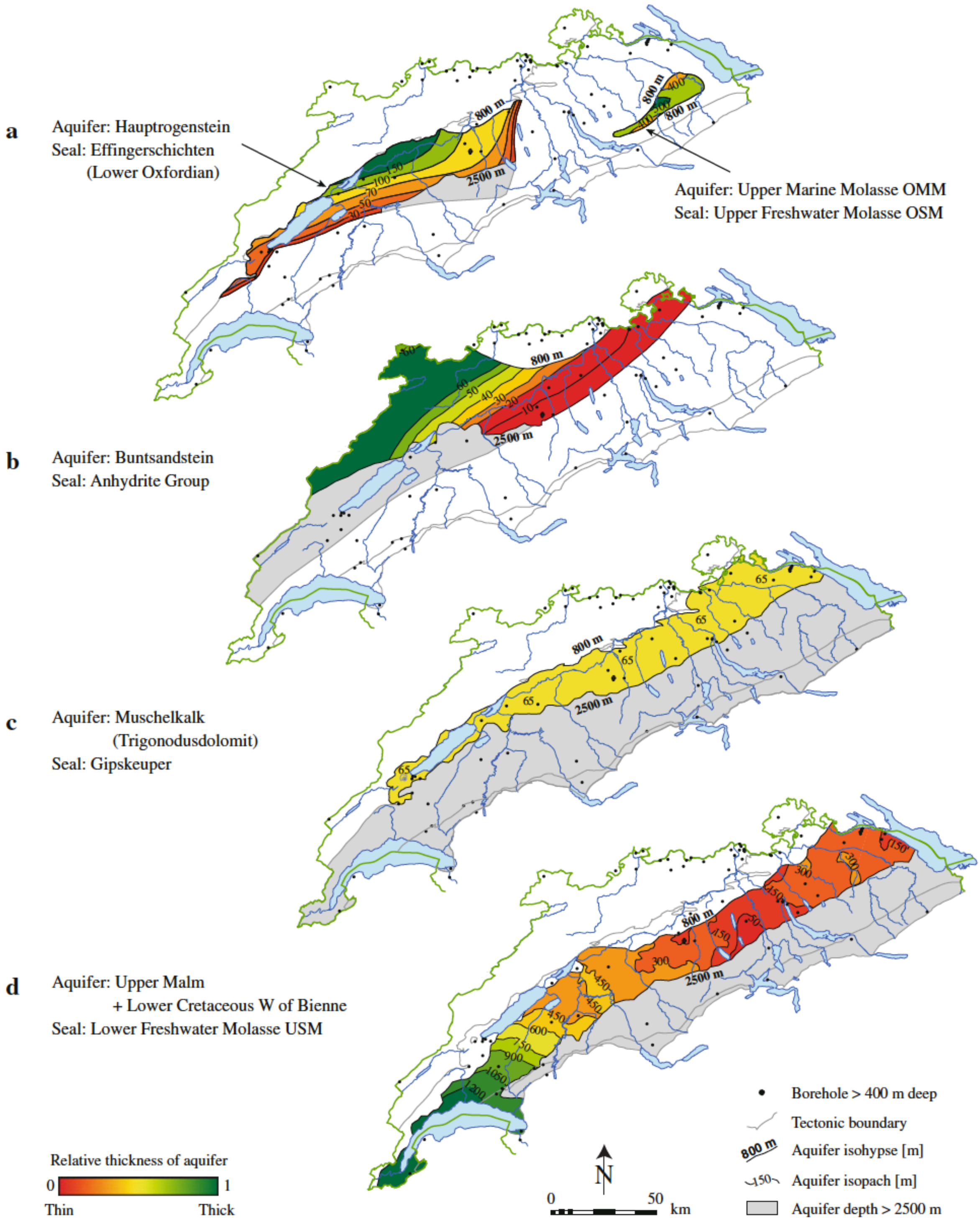

Fig. A4. Extent of five major aquifers in the Swiss Molasse Basin and the adjacent Jura fold-and-thrust belt at depth (>800 m), (Chevalier et al. 2010).

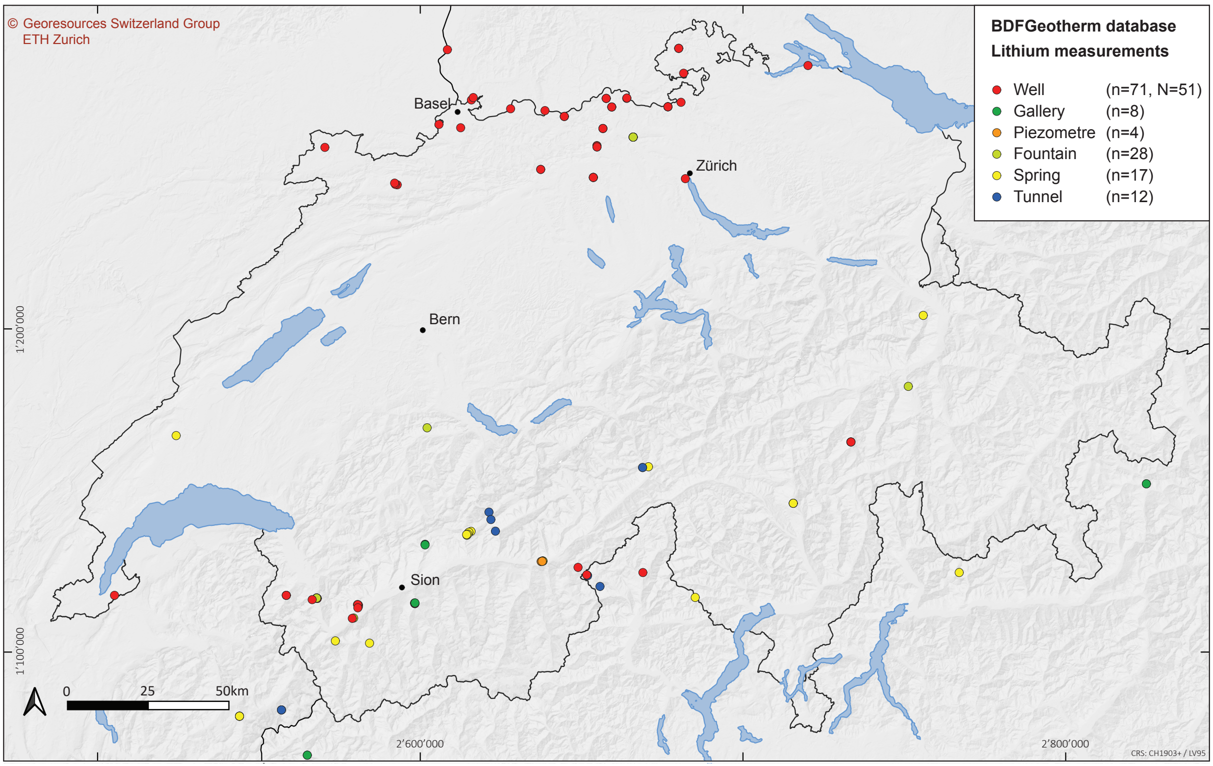

Fig. A5. Compilation of the BDFGeotherm data showing the sites/samples where lithium concentrations were measured. Among those, there are 51 well sites with 71 measurements (red circles) sites. Note that only 49 of those 51 well sites were used in our compilation – at two sites we combined two wells into one.

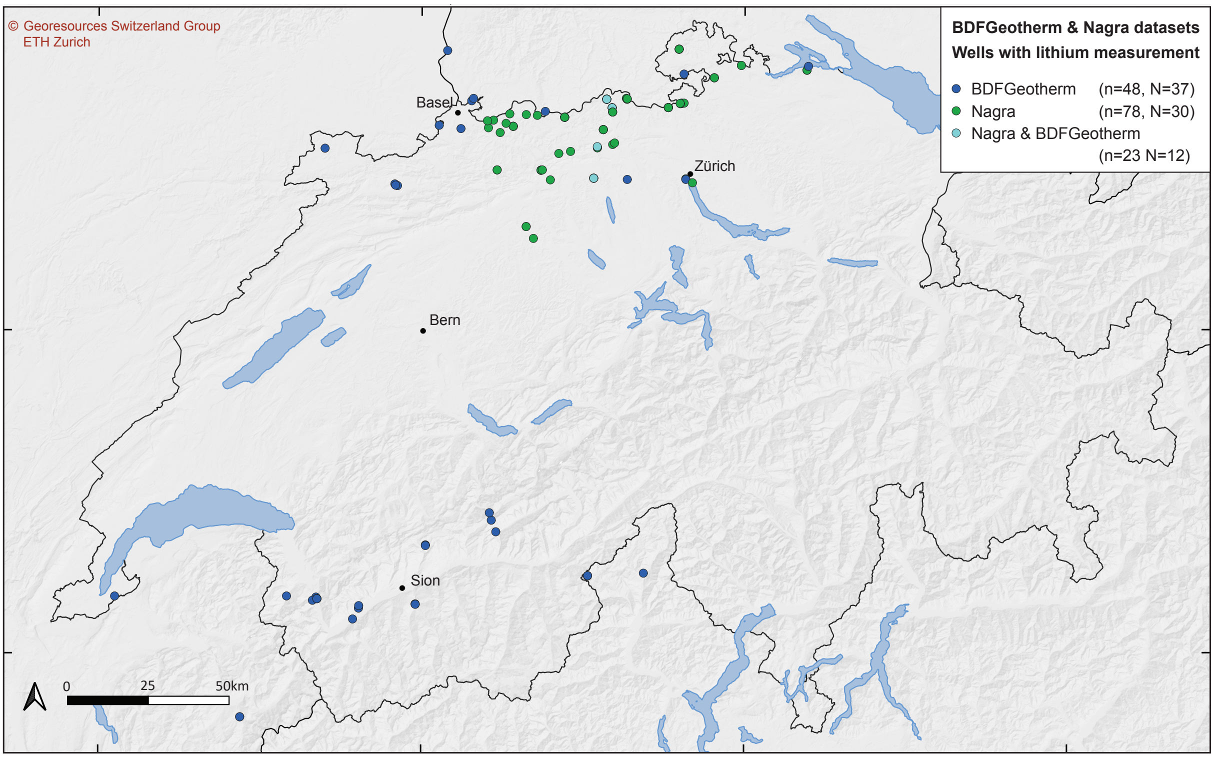

Fig. A6. Compilation of the combined BDFGeotherm and Nagra well data with lithium concentrations. Note that 12 wells with 23 measurements are present in both databases.

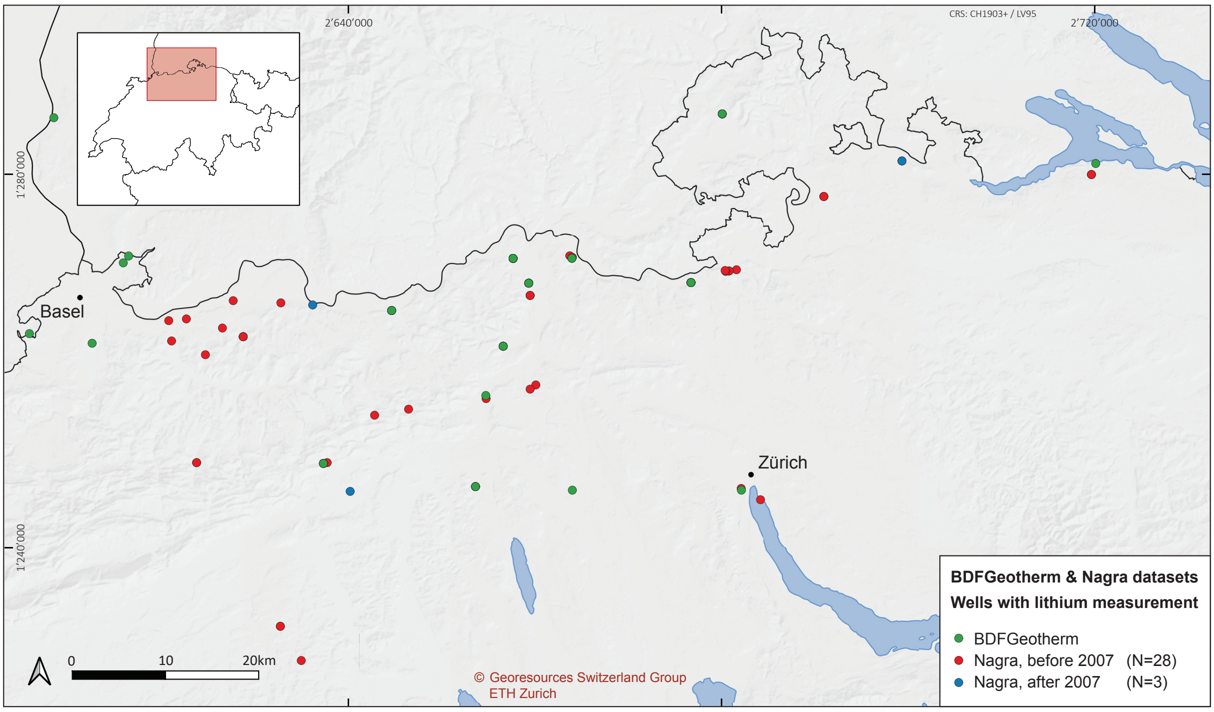

Fig. A7. Compilation of well sites in the Nagra study area illustrating that 28 wells (red circles) assembled by Nagra were not included in the BDFGeotherm database. Note that BDFGeotherm wells (green circles) are plotted on top of the Nagra-assembled wells. For well sites that occur in both databases, only the BDFGeotherm one is visible.

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