Nänikon
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Dr. Angela Hammer

Energy Storage

Specific heat capacity of rocks used for high-temperature thermal-energy storage

METTLER TOLEDO

Agenda

1 Introduction
2 Instrumentation
3 Samples
4 Results
5 Summary
6
7
8
9

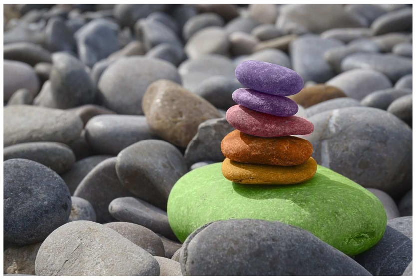
Compressed air storage power plant

- In a compressed air storage power plant, ambient air is compressed with excess current and fed into the cavern. If necessary, one reverses the flow and directs the compressed air to a turbine that drives an electricity generator. A combination of **stones and metal alloy** is used for energy storage.

Die Druckluftkaverne der Pilotanlage in einem alten Stollen bei Biasca. (Bild: Karin Hofer / NZZ)

High-temperature packed-bed thermal-energy storage.

- Different types of rocks were investigated for their suitability for high-temperature packed-bed thermal-energy storage.
- For this, the rocks were thermally cycled and the cp of the fresh samples and after cycling was recorded.
- In additon, the porosity and degree of cracking, fracturing, and disintegration were determined.



Agenda

1 Introduction
2 Instrumentation
3 Samples
4 Results
5 Summary
6
7
8
9

Instruments

TGA/DSC 3+

DSC 3+

Temperature Modulated DSC: TOPEM

TMDSC Product Positioning

IsoStep	ADSC	TOPEM®
▪ Accurate c_p using sapphire standard ▪ Kinetic effects separated from changes in heat capacity	▪ Separation of super- imposed effects at one frequency	▪ Unique multi-frequency technique ▪ Separation of super- imposed effects ▪ best c_p data
Simple & well known	Single Frequency	Multi-Frequency

Agenda

1 **Introduction**

2 **Instrumentation**

3 **Samples**

4 **Results**

5 **Summary**

6

7

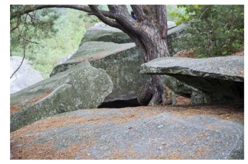
8

9

Introduction

Analyzed samples

- **Sand stone** (different minerals, mainly quartz)
- **Fontainebleau** (sandstone)
- **Felsic rock** (igneous rock formed from feldspar and quartz (silica))
- **Limestone** (CaO_3)
- **Gabbro** (coarse-grained, mafic, intrusive, igneous rock formed from the slow cooling of magnesium-rich and iron-rich magma into a holocrystalline mass deep beneath the Earth's surface)



Agenda

1. Introduction
2. Instrumentation
3. Samples
4. Results
5. Summary
6.
7.
8.
9.

Experimental

DSC

- **Goals:**
  Determine cp of different rocks by TOPEM
- **Experiment:**
- Platinum crucibles, 30 uL
- Pretreatment: isothermal drying at 105 °C for 12 h to remove absorbed water
- Cycling in TGA/DSC:
  - 5 cycle times between 100 °C and 750 with 20 K/min to simulate load and unload process
- DSC:
  - TOPEM: underlying heating rate of 2 K/min with the default parameters (pulse height: 1 K, pulse width: 15 … 30 s). For heat flow adjustment: sapphire discs (about 95 mg) using the same conditions
  - Temperature range; 200-700 °C
  - Sample: cut rocks to appropriate size of 50 to 85 mg
- **Evaluation**
  - TOPEM evaluation with adjustment using sapphire

Results

Quartz

Quartz is the main compound of most of the rocks. It can exist in different phases.

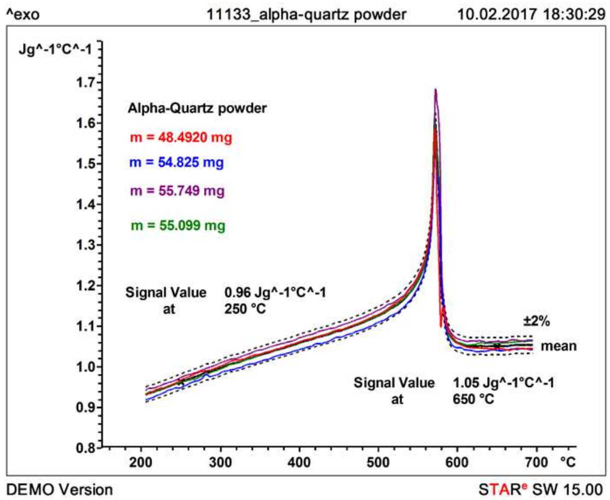
A quartz powder was measured to get an impression of c_p **repeatability using TOPEM**.

c_p curves of **four individual measurements** are displayed.

At 573 °C a-quartz undergoes a reversible change in the crystal structure to form β-quartz. This phenomenon is called inversion. The α- to β-quartz inversion is accompanied by a linear expansion of 0.45% and a peak in the specific heat capacity.

The thick black line is the average curve of the individual curves. All c_p curves are within a range of ± **2%**. This illustrates the high repeatability of this technique over such a large temperature range of more than 500 K up to 700 °C.

Results

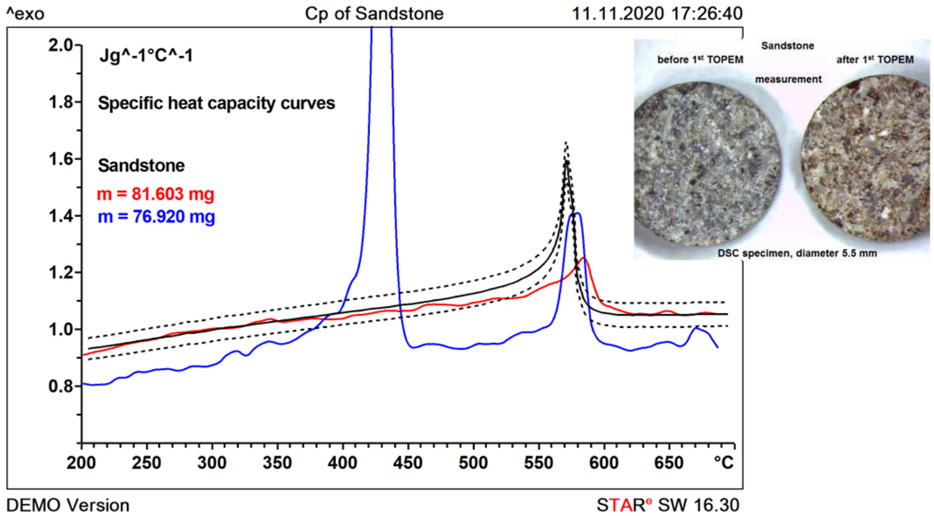


Results

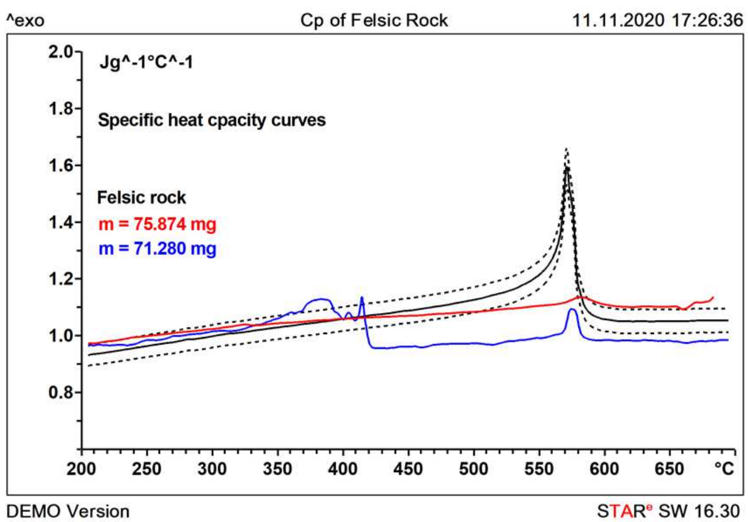
Evaluation

- c_p curves of the individual rocks measured with **TOPEM** for the fresh specimen (**red**) and after cycling (**blue**).
- For comparison, the mean c_p from a-quartz (**thick black line**) is given with its ± 4% deviation (**dotted black lines**)

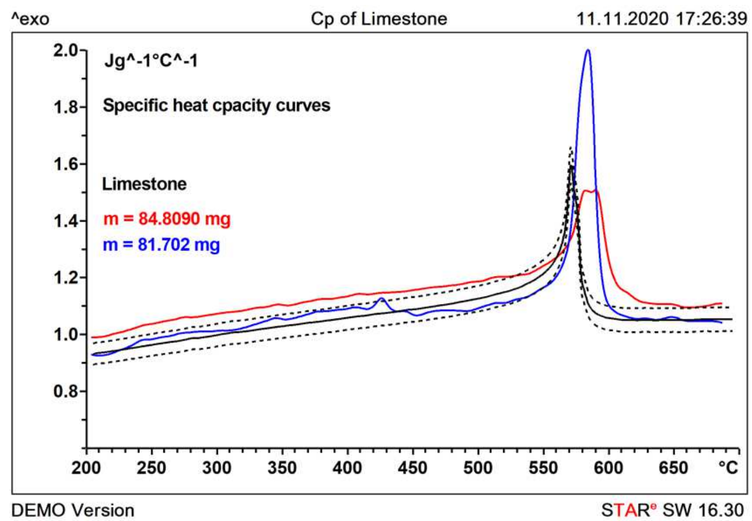
Results



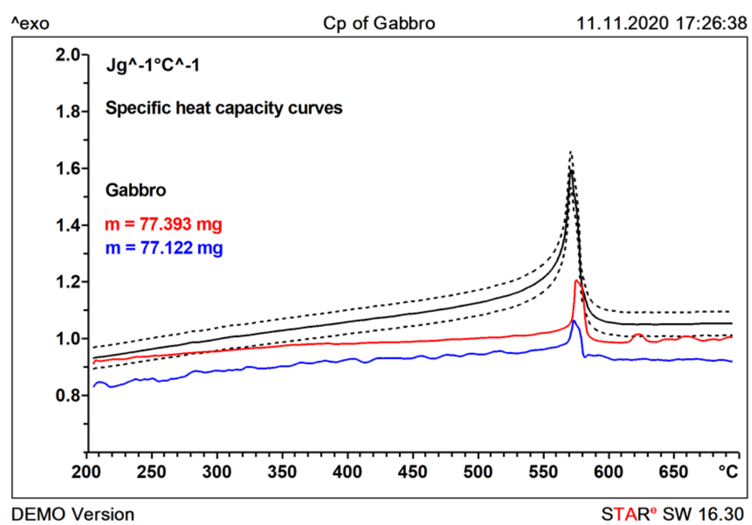
Results

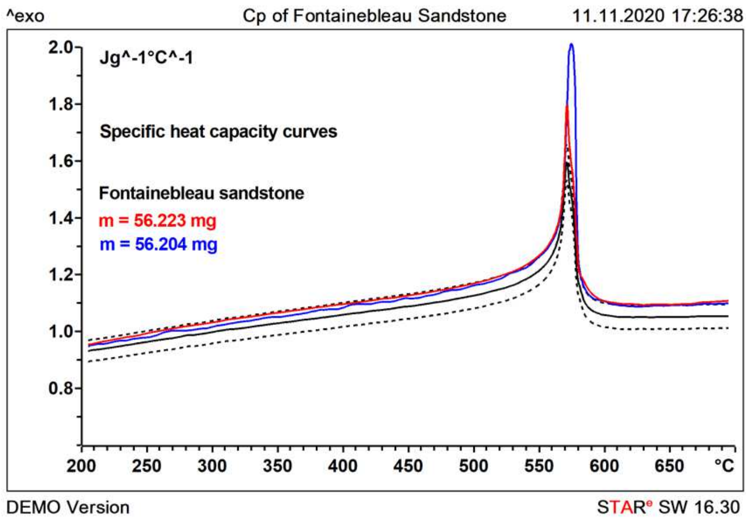


Results



Results





- With an uncertainty **of 4%**, the specific heat capacities of the fresh rock samples are basically equal to a-quartz except for Gabbro.
- During cycling different changes occur in the samples, like mass losses up to 14% for Felsic rock or color changes. These changes can be explained by physical and chemical reactions such as mineral dehydration, deserpentinization, decarbonation [1].
- During cycling, we observed **a decrease of the c_p** for most of the rocks. Only Fontainebleau shows no changes after cycling which means no mass loss, no color changes, no changes in the specific heat capacity, and no low temperature transition. Unfortunately, the quartz content is large (large a-b quartz transformation). That means risks of fragmentation caused by the change of the length (increase in the coefficient of thermal expansion CTE) during the quartz inversion.

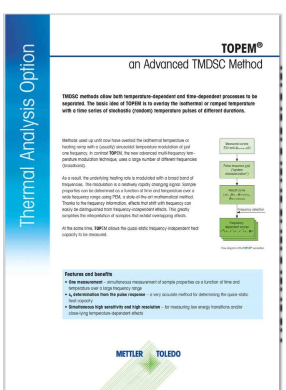
Agenda

1	**Introduction**
2	**Instrumentation**
3	**Samples**
4	**Results**
5	**Summary**
6	
7	
8	
9	

Summary

cp of rocks

- **TOPEM** is a good method for c_p determination. As TOPEM is implemented for DSC only, the highest available temperature is 700 °C.



Summary

cp of rocks

- Thermal cycling leads
  - to decreases in the specific heat capacity and
  - increases in the porosity of the rocks.

- Rocks rich in **calcite and/or quartz**, such as **limestones and sandstones**, were found to be **unsuitable** when exposed to temperatures higher than about 600 °C or 573 °C because of cracks.

- **Mafic rocks, felsic rocks, serpentinite, and quartz-rich** conglomerates are suitable for high-temperature thermal-energy storage.

- **Fontainebleau sandstone** was found as the best choice of the measured rocks if the temperature is kept below 550 °C:
  - It has the highest energy storage capacity
  - No reduction after cycling
  - Below 550 ° no quartz inversion

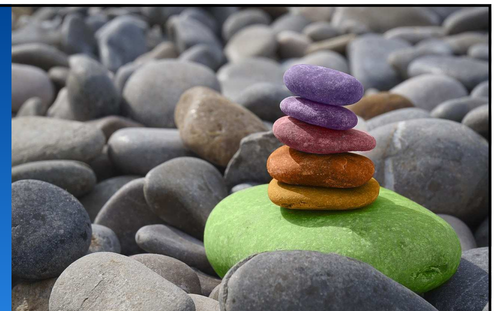
Summary

Cp of rocks

- The decreased specific heat capacity after cycling does not lead to a significant reduction in the storage capacity of packed-bed storage. Therefore, rocks that exhibit significant decreases in the specific heat capacity due to thermal cycling do not necessarily have to be regarded as unsuitable storage materials [1].

- [1] Experimental investigation of the thermal and mechanical stability of rocks for high-temperature thermal-energy storage, Applied Energy, 203 (2017) 373-389, V. Becattini et al.

- **Dr. Elke Hempel**



Thank you

The TGA/DSC 3+ is available in three modular versions

TGA/DSC 3+ features

- Small Furnace
- RT to 1100 °C
- SDTA

- Large Furnace
- RT to 1100 °C
- SDTA, DTA, DSC

- Large Furnace
- RT to 1600 °C
- SDTA, DTA, DSC

DSC 3+: Excellence Line

With or without sample robot in several modular versions

DSC 3+ options:

- –150 to 500 or 700 °C
- FRS 6+ or HSS 9+
- Excellence furnace
- Automatic furnace lid
- Sample robot
- SmartSens terminal with One Click™ function
- Built-in gas controller