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Thermosonimetric (TS) investigation of Quartz → Cristobalite - Conversion in Quartzites

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Abstract

The method of thermosonimetry (TS)[1] is used to detect indirectly an apparent conversion time of quartz to cristobalite at 1470 °C in 3 different quartzite occurrences.

This investigation shows that the TS-technique is applicable in estimating the quality of quartzites selected from a ranging of the respective half life-time constants measured:

Spanish/Greek/Swedish = 0.5/0.8/1.2 hours

The Type of Problem

The conversion of the high temperature modification of quartz to cristobalite is known to be a slow reconstructive process. The cristobalite structure is thermodynamically stable at a temperature level of 1470 °C and above. However, the rate of transition at this equilibrium temperature is physically influenced by impurities, imperfections etc., included in the chemical environment. This is the situation in the case of naturally occurring quartzites where the chemical composition may differ from ore to ore. In that respect the process of growing cristobalite crystals will depend on the quality of the mineral itself. Any actual half life-time observed for the reaction would then be a controlling measure of the degree of purity of the specific mineral, and certain decisions for further application could be taken.

Aim and Method of the Measurements

The structure of quartz and cristobalite is by itself quite different, and therefore demands a sufficient time in proceeding the transition. In a composite material like quartzites, an extra added excitation energy is needed, followed by a change in the conversion time of the process. The aim of this research is to evaluate indirectly, by use of the method of thermosonimetry, the total time necessary to overcome the influence of this extra energy barrier in crushed quartzites fired in vari-

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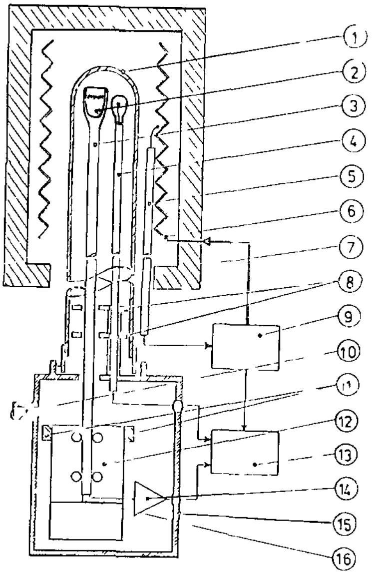
able periods of time at the conversion temperature. The sample is afterwards cooled down and reheated by a rising temperature at constant rate. A fresh sample which has not been exposed to a temperature above 900 °C, does not indicate any trace of cristobalite, as the recordings given in figure 2 show. This is in contrast to what happens to the material fired at 1470 °C shown in figure 3.

The degree of transforming the constituent of quartz to cristobalite is determined by comparing the "peak-area" of the quarts inversion at the temperature of 573 °C and that of the cristobalite deformation at about 260 °C. The difference in the quality of quartzites is then proposed to be expressed by: a) variations in the time of conversion, b) changes in the value of activation energy, and c) the choice of a theoretical model for the transition.



THE EXPERIMENTAL SET-UP.

1. PROTECTION TUBE OF ALUMINA
2. SAMPLE
3. STETHOSCOPE.
4. CHROMEL-ALUMEL THERMOCOUPLE
5. FURNACE THERMOCOUPLE
6. HEATING ELEMENT KANTHAL A
7. FURNACE.
8. RADIATION SHIELDS.
9. TEMPERATURE CONTROL SYSTEM.
10. INLET FOR ATMOSPHERIC CONTROL.
11. SEISMIC MOUNT OF THE PICK-UP SYSTEM.
12. STETHOSCOPE MOUNTING AND CELL BASEMENT.
13. AMPLIFIER-SYSTEM.
14. PRE-AMPLIFIER.
15. VACUUM SEALED HOUSING OF THE PICK-UP SYSTEM.
16. PIEZOELECTRIC CELL.

Figure 1. A scheme of the experimental set-up used for the thermosonic detection.

Experimental set-up

The fundamental apparatus for thermosonic recording is shown in figure 1. The thermo-mechanical interactions going on in the sample are picked up by the stethoscope system and converted to electrical signals. These consists of separated and short decaying pulses (bursts), which can be counted and the rate of these defined as TS-ACTIVITY, (or a kind of reaction parameter),

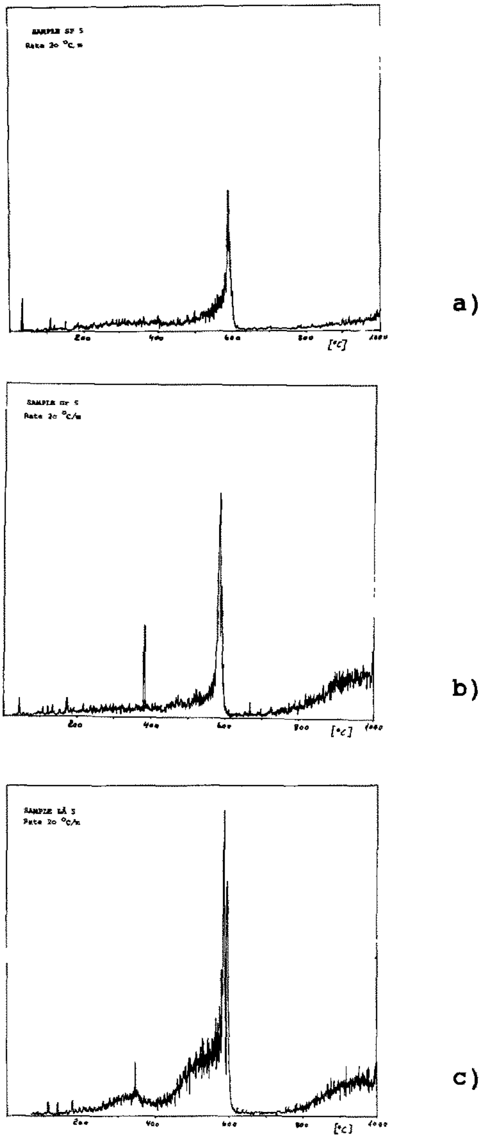
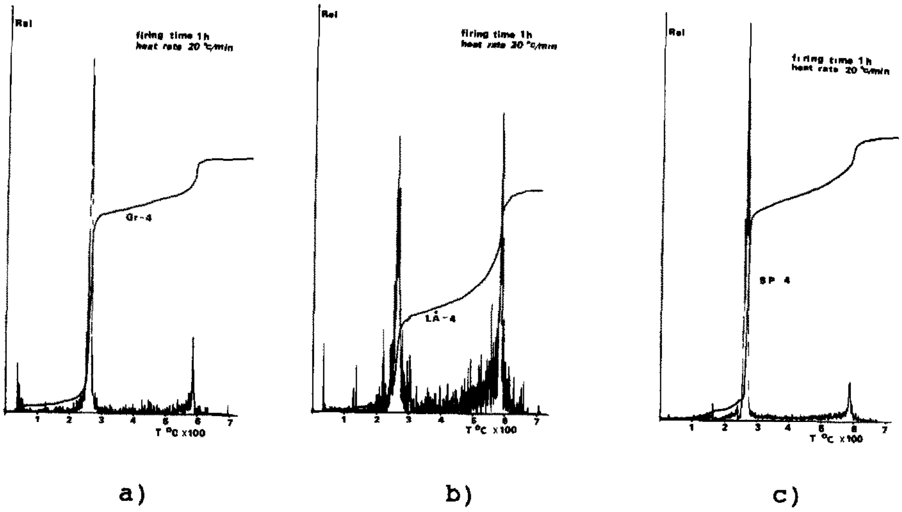


Figure 2. The characteristic shape of the thermosonic activity as a function of the temperature level of the crusted quartzites as powder samples, detected before any firing have been taken place. The respective materials are taken from ores in:

a) Spain (Sp 5),
b) Greece (Gr 5) and
c) Sweden (Lå 5).

The respective pattern shows clearly "fingerprints" of typical differences which originates from impurities and defects (Glimmerite inclusions etc. from 900 °C and upwards, decrepitations in the temperature region 300-400 °C).

as a function of the temperature level (calibrated according to the reference dummy and the temperature of the sample). (Fig.2).



a) b) c)

Figure 3. Typical thermosonic recordings (in differential and integral performance) of three samples of quartzites originating from:

a) Greece (Gr-4), b) Sweden (Lå-4) and c) Spain (Sp-4).

The crusted samples are here preheated at 1470 °C for one hour and cooled down to room temperature prior to the temperature rising measurements. Such recordings are also taken at a firing time of 2 hours.

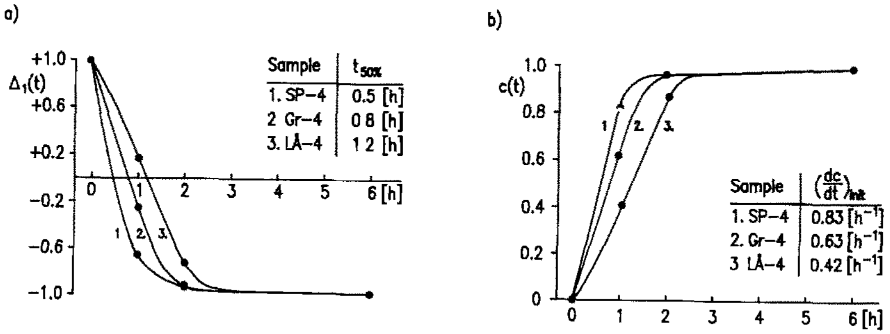


Figure 4. a) and b)

Figure 4. c)

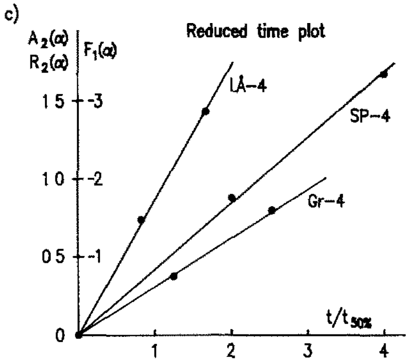


Figure 4. A graphical presentation of the evaluated experimental readings for decision of the half life-time and the rate of conversion. The curves in a) show the defined figure of merit (reaction coordinate) for the respective samples as a function of the firing time in hours. The curves in b) present the relative degree of conversion as depending on the firing time in hours. The curves c) expresses a fit to a supposed kinetic equation of the reaction by using the technique of reduced-time plot. (Confer with appendix).

Conclusion

In this investigation is 3 quite different occurrences of quartzites chosen to be measured by THERMOSONIMETRY:

Gr = from a Greek, Lå = Swedish (Lånban) and Sp = Spanish ore.

The quality of these 3 minerals is experienced to be different. In that sense the outcome of the TS-detection should show variations in the pattern of the recorded curves (see figure 2), and in the derived values of the factor of merit (see appendix) describing the conversion time response (see figure 4). The period of time for 50 % conversion is respectively calculated to be:

Sp/Gr/Lå = 0.5/0.8/1.2

which is ranged in accordance to the experience of a "good" quartzite (close to pure quartz) from Sp to the less beneficent one from Lå. An apparent "conversion" rate-factor initially is deduced from the curves to be:

Sp/Gr/Lå = 0.83/0.63/0.42 per hour.

The reduced time plots clearly show that the different amount of impurities in the quartzites lead to variations in the character of conversion (see appendix), and that alternative theoretical models can be choosen. A corresponding result is given by the difference on in the activating energy.

These results show that the quality of quartzites can be evaluated and that descriptive parameters of the conversion mechanism of quartz to cristobalite can be given by using the technique of Thermosonimetry.

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APPENDIX (data calculations)

1. General concept

The working data are read from curves of the integrated TS-activity given by the count number: N_1, N_2, and N_3, at the respective temperatures: 200 °C, 300 °C and 620 °C. A primary reaction on the conversion is defined by the factor

$f(t) = (N_2 - N_1)/(N_3 - N_1)$; t = firing time in hours.

This factor has to be normalized with respect to the limiting conditions:

1) no firing time turns out in 0 % conversion,
2) long firing time leads to 100 % conversion.

The relative yield of the converted fraction is then written as:

$$\Delta_1 = [\, f(6) + f(0) - 2\, f(t)] \;/\; [\, f(6) - f(0)]$$

and the degree of conversion expressed by the formula:

$$\underline{c(t) = [\, 1 + \Delta_1(t)] /2}\ .$$

The calculated values are presented in figure 4.

2. Thermo-kinetic valuation.

The change property P(t) of a substance with time can be formulated by the following rate equation of balance:

$$dP(t)/dt = -A.P(t)^n \,.\, \exp(-E/kT) \quad ,$$

where n means the order of reaction, E the activation energy and A a frequency factor. By supposing the same level of property (degree of conversion), the difference in the actual energy of activation for these types of materials will be given by the relation:

$$\text{diff. } E = E_1 - E_2 = k.T.\ \ell n(t_1/t_2)_{50\%} = E_x - E_{Sp}.$$

The conditional calculation based on this assumption will result in the following values:

Sample	$t_{50\%}$ [h]	diff.E [eV]	
Sp	0.5	0.0	(Reference)
Gr	0.63	0.0238	
Lå	1.2	0 0903	

The statistical formula for variation in property of a substance can also be organized to have the fraction $\alpha = P(t)/P(0)$ separated by introduction of the relative reduced time coordinate $r = (t/t_{50\%})$. This manipulation leads to two equal but formally independent functions:

$F_n(\alpha) = k.(r)$,

where $t_{50\%}$ corresponds to the fraction $\alpha = 0.5$. The corresponding data are shown in figure 4c. $F_n(\alpha)$ is based on theoretical models of possible reaction pattern.

The numerical value of such functions are tabulated for different parametric values of n as a function of the fraction yield α . The result of direct numeric comparison and fit of these functions are given in the table below:

Sample	Calculated (formula)	k_{exp}	Model	k_{theo}	Order of $_n$
Gr	$1-(1-c)^{½}$	0.322	$R_2(\alpha)$	0.293	2
Sp	$\ell n(1-c)$	0.842	$F_1(\alpha)$	0.693	1
Lå	$\ell n(1-c)^{½}$	0.860	$A_2(\alpha)$	0.833	2

$F_1(\alpha)$ reflects on a first order decay-model, as $A_2(\alpha)$ describes a reaction of second order and $R_2(\alpha)$ related to a two-phase surface reaction. (The used theoretical values are taken from tables in the book: "Introduction to Thermogravimetry", by Dr.Prof. D. Bollimore.)

REFERENCE

[1] Thermochemica Acta, 110 (1987) 253-264.