Measurement of thermal expansion coefficient of rock minerals using XRD and its implications to thermal damage mechanism

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Abstract. The measurement of thermal expansion coefficient (TEC) of rocks is of vital importance to various geotechnical engineering applications, such as high-level radioactive waste disposal, enhanced geothermal energy exploitation, ultra-deep borehole stability, liquid nitrogen storage, etc. However, previous researchers mainly focused on the thermal expansion coefficient of various rocks, instead of the constituent minerals. In this manuscript, we measured the both temperature-dependent volume and linear thermal expansion coefficients of two rock-forming minerals (quartz and albite) using both high-temperature X-ray diffraction (XRD) as well as low-temperature XRD. It is found that there exist strong anisotropic linear thermal expansion coefficients of the two minerals, which can provide strong reference for the relevant engineering applications and numerical simulations.

1. Introduction
Thermal stresses induced during the heating or cooling of rocks cause fracture and fragmentation, which is of vital importance to various geotechnical engineering applications, such as high-level radioactive waste disposal, enhanced geothermal energy exploitation, ultra-deep borehole stability, etc. Rocks are inherently heterogeneous and they are polycrystalline with various anisotropic mineral aggregates. Generally, thermal stresses can be generated due to the following reasons: (1) thermal expansion (contraction) coefficient mismatch between different phases (grains) (2) anisotropic thermal expansion (contraction) coefficient of individual phase (3) thermal gradient (heating or cooling rate) (4) phase change and/or structural chemical reactions (5) temperature-dependent elastic modulus of each individual phase (6) composition, distribution and orientation of individual grains (7) presence of crack or fracture (8) previous maximum temperature (9) presence of water (moisture content) (10) pressure [1] (11) thermal cycling (temperature history). Take granite for instance, it consists of three major mineral constituents, namely, quartz, feldspar and mica. The thermal expansion coefficient of these three dominant minerals is of great difference. For each single phase, there exists a distinct anisotropic linear thermal expansion coefficient, which is relatively less studied. Thermal expansion coefficient ($\alpha_V$) indicates the percentage of material expands or contracts with temperature changes. Under a constant pressure, volumetric thermal expansion coefficient ($\alpha_V$ or $\beta$) is defined by the variations of volume by a differential temperature change ($\Delta T$) and it is normally described as the following relationship:

$$\alpha_V = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

where $V$ is the volume at a temperature $T$ under a constant pressure $P$. 
Similarly, the linear thermal expansion coefficient is defined as:

\[ \alpha_l = \frac{1}{l} \left( \frac{\partial l}{\partial T} \right)_P \]

Accurate thermal expansion coefficients of rock-forming minerals are of great essence to the clarification of the equation of state of the earth’s interior [2] and it is emphasized that most serious error in the calculation of thermodynamic functions arises from the uncertainty of thermal expansivity at high temperature [3]. In most cases, rocks are assumed to be homogeneous and isotropic for the convenience of analysis. Only a few studies focused on the thermal expansion coefficient measurement of rock minerals. For instance, Jay [4] measured the lattice parameters of quartz from 18 to 730 °C using the high-temperature Debye-Scherrer method and it was found that thermal expansion coefficients in both axial direction of the hexagonal unit cell increased from 18 to 580 °C and both axes apparently decreased in length from 580 to 730 °C. Ackermann and Sorrell [5] measured the thermal expansion coefficient of quartz using high-temperature X-ray diffractometry from 22 to 1400 °C. It was found that the expansion was zero from 574 to 1000 °C and decreased from 1000 to 1400 °C. The maximum volume thermal expansion coefficient was 100 ± 20 × 10^{-5} /degree between 572 and 574 °C. In addition, they [6] measured the thermal expansion of both single-crystal quartz and quartz powder using the highly sensitive dilatometer apparatus. It was found that the expansion coefficient characteristics were identical with X-ray diffractometer measurement below 560 °C. Single-crystal quartz reached a maximum volume thermal expansion coefficient 250 × 10^{-5} /degree between 571 and 573 °C while the quartz powder reached a maximum volume thermal expansion coefficient 150 × 10^{-5} /degree between 571 and 576 °C.

Richter and Simmons [7] measured the thermal expansion coefficient of several igneous rocks from 25 to 550 °C and they found that the measured thermal expansion coefficient is a function of crack porosity, heating rate, previous maximum temperature as well as mineralogical composition and preferred crystal orientation. In their study, they only measured the linear thermal expansion coefficient of rock core along the long dimension of the sample only, and the volume expansion was assumed to be three times the linear expansion coefficient. In addition, the anisotropy of expansion was not investigated. The experimental volume expansion coefficients of the rocks and calculated value using the Turner’s formula and the input value for the Turner’s calculation is from [7]. Alvaro, Angel et al. [8, 9] measured the unit cell volume of quartz using the high-temperature single-crystal X-ray diffraction from 294K to 872K.

2. Temperature Calibration

In this manuscript, the thermocouple measurements were calibrated using the lattice parameter changes for magnesium oxide (MgO) as a function of the temperature. We measured the XRD pattern of MgO with the change of temperature, as shown in figure 1. It can be found that there is an obvious peak shift of MgO in the temperature range between room temperature and 1200 °C. Figure 2 demonstrated the calibrated temperature of MgO with the set temperature and it can be found that the two curves fit very well, which indicates the accuracy of temperature.
3. XRD experimental results for quartz and albite

3.1 Thermal expansion coefficient and unit cell parameters of quartz

Figure 3 demonstrates the XRD pattern of quartz from room temperature to 1200 °C and figure 4 shows the magnification of XRD pattern of quartz from room temperature to 1200 °C. Linear and volume expansion coefficients are calculated using the following equation:

$$\alpha_i = \frac{1}{1 + \frac{\Delta Y_i}{\Delta T}}$$

where the suffix \(i\) represents a, b, c (each crystallographic axis) and \(v\) (volume). The unit cell parameters of quartz under various temperatures were gained using the Rietveld method and the results are shown in Table 1.
Figure 3. XRD pattern of quartz from room temperature to 1200°C

Figure 4. Magnification of XRD pattern of quartz from room temperature to 1200°C

Table 1. Relationship of unit cell parameters of quartz with various temperatures

| Set Temperature (°C) | Calibrated temperature (°C) | Unit cell Volume (Å³) | Unit Cell Volume Error | a (Å) | Error of a (Å) | c (Å) | Error of c (Å) |
|---------------------|-----------------------------|----------------------|------------------------|-------|----------------|-------|----------------|
| 30                  | 30.432                      | 112.997              | 0.0012                 | 4.9134| 0.00002299     | 5.404704| 0.00002789     |
| 60                  | 60.864                      | 113.13               | 0.001                 | 4.915654| 0.00001813    | 5.406116| 0.00002369     |
| 100                 | 101.44                      | 113.317              | 0.0009                | 4.918826| 0.00001666    | 5.408062| 0.00002655     |
| 150                 | 152.16                      | 113.569              | 0.0009                | 4.923111| 0.00001594    | 5.410651| 0.00002269     |
| 200                 | 202.88                      | 113.841              | 0.001                 | 4.927676| 0.00001818    | 5.413549| 0.00002417     |
| 250                 | 253.6                       | 114.133              | 0.0013                | 4.932559| 0.00002422    | 5.416709| 0.00002825     |
| 300                 | 304.32                      | 114.455              | 0.001                 | 4.93795 | 0.00001722    | 5.420121| 0.00003026     |
| 350                 | 355.04                      | 114.803              | 0.0011                | 4.943732| 0.00001938    | 5.423896| 0.00003268     |
| 400                 | 405.76                      | 115.194              | 0.0014                | 4.950275| 0.00002614    | 5.428004| 0.00003047     |
| 450                 | 456.48                      | 115.645              | 0.0014                | 4.957828| 0.00002224    | 5.432687| 0.00004227     |
| 500                 | 507.2                       | 116.212              | 0.0013                | 4.967182| 0.00002298    | 5.438776| 0.00003027     |
| 550                 | 557.92                      | 117.203              | 0.0019                | 4.983595| 0.00003551    | 5.44908 | 0.00004333     |
| 600                 | 608.64                      | 118.032              | 0.0018                | 4.997388| 0.00003069    | 5.457351| 0.00004623     |
| 650                 | 659.36                      | 118.027              | 0.0017                | 4.997536| 0.00002997    | 5.456792| 0.00005055     |
| 700                 | 710.08                      | 118.012              | 0.0011                | 4.99748 | 0.00001614    | 5.456229| 0.00003419     |
| 750                 | 760.8                       | 117.992              | 0.0016                | 4.997404| 0.00002594    | 5.455496| 0.00004672     |
| 800                 | 811.52                      | 117.973              | 0.0013                | 4.997257| 0.00002155    | 5.454927| 0.00003838     |
Figure 5. Unit cell parameters change of quartz from room temperature to 1200 °C

Figure 5 shows the unit cell parameters change of two directions of quartz (namely, a and c). There exists an obvious variation of unit cell parameters near the phase change temperature (namely, 573 °C). The quartz $\alpha - \beta$ transition is marked by a kink in the unit cell parameters, as shown in the above figures. From the above curves, we can find that quartz has a steep, nonlinear expansion curve until its transition temperature and a slight contraction exists beyond the transition temperature.

3.2 Thermal expansion coefficient and unit cell parameters of albite

Similarly, figure 6 demonstrates the XRD pattern of albite from room temperature to 1200 °C and figure 7 shows the magnification of XRD pattern of albite from room temperature to 1200 °C. The unit cell parameters of albite under various temperatures were gained using the Rietveld method and the results are shown in Table 2. Figure 8 shows the unit cell parameters change of three directions of albite and figure 9 demonstrates the unit cell angle variation of albite with temperature. Figure 10 shows the both the volume and linear thermal expansion coefficient of albite with the calibrated temperature and it can be seen that there exists a strong anisotropic thermal expansion coefficient of albite and both the volume and linear thermal expansion coefficient of albite increases with the temperature.
Figure 6. XRD pattern of albite from room temperature to 950 °C

Figure 7. Magnification of XRD pattern of albite from room temperature to 950 °C

Table 2. Relationship of unit cell parameters of albite with various temperatures

| Set temperature (°C) | Calibrated temperature (°C) | Volume ($\text{Å}^3$) | a (Å) | b (Å) | c (Å) | α (°) | β (°) | γ (°) |
|----------------------|-----------------------------|-----------------------|-------|-------|-------|-------|-------|-------|
| 30                   | 30                          | 664.938               | 8.143125 | 12.79024 | 7.160918 | 94.24636 | 116.6172 | 87.74094 |
| 100                  | 101.008                     | 666.167               | 8.151428 | 12.79433 | 7.161221 | 94.2226 | 116.567 | 87.73409 |
| 150                  | 151.728                     | 667.03                | 8.157127 | 12.79744 | 7.161281 | 94.19119 | 116.5319 | 87.72876 |
| 200                  | 202.448                     | 668.001               | 8.163595 | 12.80085 | 7.161787 | 94.16269 | 116.4983 | 87.71893 |
| 250                  | 253.168                     | 668.877               | 8.169331 | 12.80423 | 7.162122 | 94.13197 | 116.4682 | 87.70934 |
| 300                  | 303.888                     | 669.88                | 8.175948 | 12.80755 | 7.163084 | 94.09352 | 116.4387 | 87.69948 |
| 350                  | 354.608                     | 670.88                | 8.182209 | 12.81216 | 7.163663 | 94.05622 | 116.4107 | 87.68577 |
| 400                  | 405.328                     | 671.912               | 8.188472 | 12.8164 | 7.1647 | 94.00687 | 116.383 | 87.68124 |
| 450                  | 456.048                     | 673.02                | 8.195641 | 12.82044 | 7.165916 | 93.96167 | 116.3553 | 87.67019 |
| 500                  | 506.768                     | 673.905               | 8.201536 | 12.82384 | 7.166494 | 93.90932 | 116.3329 | 87.663 |
| 550                  | 557.488                     | 675.013               | 8.208406 | 12.82798 | 7.167861 | 93.85375 | 116.3056 | 87.65198 |
| 600                  | 608.208                     | 675.949               | 8.214505 | 12.83135 | 7.168712 | 93.79725 | 116.2819 | 87.63967 |
| 650                  | 658.928                     | 677.007               | 8.221115 | 12.83528 | 7.169874 | 93.74332 | 116.254 | 87.62926 |
| 700                  | 709.648                     | 678.091               | 8.22804 | 12.83933 | 7.171152 | 93.6799 | 116.2304 | 87.61681 |
| 750                  | 760.368                     | 679.136               | 8.23472 | 12.84418 | 7.171764 | 93.61521 | 116.2066 | 87.60656 |
| 800                  | 811.088                     | 680.172               | 8.241806 | 12.84739 | 7.17293 | 93.55089 | 116.1839 | 87.59337 |
| 850                  | 861.808                     | 681.371               | 8.250021 | 12.85182 | 7.174199 | 93.47926 | 116.1627 | 87.58058 |
| 900                  | 912.528                     | 682.629               | 8.258159 | 12.85653 | 7.175586 | 93.40101 | 116.1356 | 87.57001 |
| 950                  | 963.248                     | 683.925               | 8.266808 | 12.86114 | 7.177362 | 93.31534 | 116.1153 | 87.56183 |
4. Conclusions:
In this study, the relationship between the rock mineral thermal expansion coefficient and temperature was established. The unit cell parameters (a, b, c, α, β, γ and V) were refined using the Rietveld method. For quartz, there exists an obvious variation of unit cell parameters near the phase change temperature (namely, 573 °C) and quartz has a steep, nonlinear expansion curve until its transition temperature and
a slight contraction exists beyond the transition temperature. For albite, there exists a strong anisotropic thermal expansion coefficient and both the volume and linear thermal expansion coefficient of albite increases with the temperature.

This study if of vital importance to the relevant geotechnical engineering, such as high-level radioactive waste disposal, enhanced geothermal energy extraction, etc. In addition, the accurate measurement of thermal expansion coefficients of these rock minerals can provide baselines for the numerical simulation.

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