

Thermal storage and transport Properties of Rocks, I: Heat Capacity and Latent Heat

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## THERMAL STORAGE AND TRANSPORT PROPERTIES OF ROCKS, I: HEAT CAPACITY AND LATENT HEAT

### Synonyms

Specific heat capacity; thermal capacity; volumetric heat capacity

### Definition

*Specific heat capacity  $c$ .* Physical property defining the amount of sensible heat which can be stored in or extracted from a unit mass of rock per unit temperature increase or decrease, respectively. Isobaric and isochoric specific heat capacities are defined at constant pressure and volume, respectively; dimension:  $\text{J kg}^{-1} \text{K}^{-1}$

*Thermal capacity (also: volumetric heat capacity)  $\rho c$ .* The product of isobaric specific heat capacity and density. Physical property defining the amount of sensible heat which can be stored in or extracted from a unit volume of rock per unit temperature increase or decrease, respectively; dimension:  $\text{J m}^{-3} \text{K}^{-1}$ .

### Thermal storage properties

The thermal regime of the Earth is defined by its heat sources and sinks, the heat storage and transport processes and their corresponding physical properties. The storage properties are discussed below. The transport properties, thermal conductivity and thermal diffusivity, are dealt with in this volume in the companion chapter “Thermal Storage and Transport Properties of Rocks, 2: Thermal conductivity and diffusivity”.

Heat can be stored as sensible heat and enthalpy of transformation. In the Earth, sensible heat is defined by the heat capacity of rocks, and the enthalpy of transformation by their latent heat of fusion.

Heat is transmitted within the Earth mainly by diffusion (in the steady-state: conduction), advection, and radiation. Generally, heat diffusion dominates heat radiation within the lithosphere of the Earth, at temperatures below about 1 000 K. For sufficiently large flow rates convection driven heat advection, however, can be equally or even more efficient than diffusion. The heat diffusion-advection equation for a porous medium is:

$$\frac{\partial(\rho c_p T)}{\partial t} = \nabla \cdot \left( \underbrace{\lambda \nabla T}_{q_{\text{dif}}} - \underbrace{(\rho c_p)_f T \mathbf{v}}_{q_{\text{adv}}} \right) + \underbrace{\dot{A}}_{\text{generation}}, \quad (1)$$

where  $T$  is temperature in K,  $t$  time in s,  $\rho$  density in  $\text{kg m}^{-3}$ ,  $c$  isobaric specific heat capacity in  $\text{J kg}^{-1} \text{K}^{-1}$ ,  $\lambda$  thermal conductivity in  $\text{W m}^{-1} \text{K}^{-1}$ ,  $\mathbf{v}$  specific fluid discharge (volume flow rate per unit cross-section) in  $\text{m s}^{-1}$ ,  $\dot{A}$  (radiogenic) heat generation rate in  $\text{W m}^{-3}$ ; subscript “f” refers to fluid properties. Diffusive bulk storage and transport properties for heat in rocks governing this equation are thermal capacity  $\rho c_p$ , also referred to as volumetric heat capacity,

and thermal conductivity  $\lambda$ . Advection is governed by the thermal capacity and specific discharge of the flowing fluid,  $(\rho c_p)_f$  and  $v$ , respectively.

Heat advection does not require very large flows for becoming as or more efficient than heat diffusion. This is often the case in sedimentary basins (see e.g. Clauser et al. (2002) for a literature review). But fluid driven heat advection may be also important in crystalline rocks and on a crustal scale (e.g. Clauser, 1992). The non-dimensional Péclet and Nusselt numbers,  $Pe$  and  $Nu$ , are ratios of specific heat flows  $q_{adv}$  and  $q_{dif}$  (1) indicating the efficiency of (fluid flow driven) advective heat transport versus heat conduction for given flow geometries. For instance, assuming flow of magnitude  $v$  over a distance  $L$  and a temperature difference  $T_1 - T_0$  one obtains:

$$\begin{aligned} Pe &= \frac{q_{adv}}{q_{dif}} = \frac{(\rho c)_f v (T_1 - T_0)}{\lambda (T_1 - T_0)/L} = \frac{(\rho c)_f v L}{\lambda}, \\ Nu &= \frac{q_{adv} + q_{dif}}{q_{dif}} = \frac{q_{adv}}{q_{dif}} + 1 = Pe + 1. \end{aligned} \quad (2)$$

Thus advection or diffusion (in the steady state: conduction) dominate for  $Pe > 1$  or  $Pe < 1$ , respectively (in terms of the Nusselt number for  $Nu > 2$  or  $Nu < 2$ , respectively). At temperatures above 1000 K, heat is propagated increasingly as radiated electromagnetic waves, and heat radiation begins to dominate diffusion (see the companion article “Thermal Storage and Transport Properties of Rocks, II: Thermal Conductivity and Diffusivity” in this volume).

## Heat capacity

Heat can be stored and delivered as sensible heat or as latent heat required or liberated by phase changes. This and the next two paragraphs are concerned with sensible heat. Following this, latent heat will be discussed.

Sensible heat capacity  $C$  is defined as the ratio of heat  $\Delta Q$  required to raise the temperature of a mass  $M$  of rock by  $\Delta T$ . For each molecule of mass  $m$  this temperature increase requires an energy of  $(f/2) k \Delta T$ , where  $f$  is the number of degrees of freedom of the molecule and  $k = 1.380\,650\,4(24) \times 10^{-23} \text{ J K}^{-1}$  is Boltzmann's constant. For a body of mass  $M$  a temperature increase of  $\Delta T$  requires an energy of  $\Delta Q = (M/m) (f/2) k \Delta T$ . Thus the heat capacity of the body at constant volume is:

$$C_v = \frac{\Delta Q}{\Delta T} = \frac{f}{2} k \frac{M}{m} = \frac{f}{2} k N_A = \frac{f}{2} R \quad (\text{J K}^{-1}), \quad (3)$$

where Avogadro's number  $N_A = 6,022\,141\,79(30) \times 10^{23} \text{ mol}^{-1}$  equals the number of molecules or atoms in an amount of substance of 1 mol and  $R = k N_A = 8,314\,472(15) \text{ J mol}^{-1} \text{ K}^{-1}$  is the molar Gas constant (numerical values for  $N_A$ ,  $R$ ,  $k$ , and all other physical constants used in this chapter are from CODATA, 2006). For solids,  $f=6$ , corresponding to the three degrees of freedom of potential and kinetic lattice vibration energy in each space direction. Accordingly, the heat capacity of one mole of substance, the molar heat capacity at constant volume is constant:

$$C_{v,\text{mol}} = 3k N_A = 3R = 24.94 \text{ (J mol}^{-1} \text{ K}^{-1}) \quad (4)$$

where  $N_A = 6.022\,141\,79(30) \times 10^{23} \text{ mol}^{-1}$  is Avogadro's number, the number of molecules in one mole of substance, and  $R = k N_A$  the molar gas constant. Isobaric heat capacity  $C_{p,\text{mol}}$  is larger than isochoric heat capacity  $C_{v,\text{mol}}$  because additional work is required for volume expansion. Both are related by:

$$C_{P,\text{mol}} = C_{V,\text{mol}} + R = \frac{f+2}{2} R \quad (\text{J mol}^{-1} \text{K}^{-1}). \quad (5)$$

With  $C_{V,\text{mol}}$  from (4) and assuming, as above,  $f=6$  this yields:

$$C_{P,\text{mol}} = 3R + R = 4R = 33.26 \quad (\text{J mol}^{-1} \text{K}^{-1}), \quad \text{or: } C_{P,\text{mol}} - C_{V,\text{mol}} = R. \quad (6)$$

Equation (4), the *Dulong-Petit law*, is satisfied well for heavy elements. In contrast, molar heat capacities of lighter elements remain below this limiting value, the lower the temperature the smaller  $C_{V,\text{mol}}$ .

**Tab. 1 Debye temperature  $\Theta_D$  and mass number A of selected elements (Kittel, 2004).**

Element	Mass Number A	$\Theta_D$ (K)	Element	Mass Number A	$\Theta_D$ (K)
carbon	6	2 230	zinc	30	327
aluminum	13	428	silver	47	215
silica	14	645	Cadmium	48	209
titanium	22	420	tin	50	200
chromium	24	630	tantalum	73	240
manganese	25	410	tungsten	74	400
iron	26	470	platinum	78	240
nickel	28	450	gold	79	165
copper	29	343	lead	82	105

Below the Debye temperature,  $\Theta_D$ , heat capacity varies with temperature.  $\Theta_D$  tends to zero as  $T^3$  as absolute temperature approaches zero.  $\Theta_D$  falls in the range 85 K and 450 K for most substances and 200 K and 1 000 K for most minerals (Stacey & Davis, 2008; Tab. 1). Therefore, heat capacity in the Earth can be well explained by classical Debye theory, in particular in the mantle and except for a thin crustal layer near the Earth's surface. There are, however, exceptions such as beryllium ( $\Theta_D = 1\,440$  K) and diamond ( $\Theta_D \approx 1\,800$  K). These are caused by the so-called freezing of vibrational or rotational degrees of freedom, which cannot absorb heat any more at low temperature. Therefore heat capacity tends to zero close to absolute zero.

### Isobaric and isochoric specific heat capacity

Specific heat capacity  $c$  of a substance is defined as heat capacity  $C$  related to unit mass:

$$c = \frac{\Delta Q}{M \Delta T} = \frac{f}{2} \frac{k}{m} = \frac{f}{2} \frac{k}{A_r m_u} \quad (\text{J kg}^{-1} \text{K}^{-1}), \quad (7)$$

where  $m_u = 1.660\,538\,782(83) \times 10^{-27}$  kg is the atomic mass constant, defined as  $1/12$  of the atomic mass of the carbon isotope  $^{12}\text{C}$ , and  $A_r$  the atomic mass of a substance relative to  $m_u$ . Isobaric specific heat capacity  $c_p$  is larger than isochoric specific heat capacity  $c_v$  because additional work is required for volume expansion. Their ratio, the adiabatic exponent, is:

$$c_p / c_v = (f+2) / f. \quad (8)$$

Alternatively, isobaric specific heat capacity  $c_p$  can be expressed by enthalpy  $H(T,P) = E + P V$ , a state function of temperature and pressure, where  $E$ ,  $P$ , and  $V$  are internal energy, pressure, and volume, respectively. In a closed system, the change in internal energy  $dE$  is the sum of the change in heat  $dQ$  and the work  $dW$  delivered:  $dE = dQ + dW$ . If we only consider volume expansion work:  $dW = -P dV$ , the change in enthalpy  $dH$  becomes:

$$dH(T, P) = dE + p dV + V dP = dQ + V dP = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP. \quad (9)$$

Comparing coefficients, we obtain:

$$\frac{dQ}{dT} = \left( \frac{\partial H}{\partial T} \right)_P \doteq c_P. \quad (10)$$

Thus, eq. (10) defines isobaric specific heat capacity  $c_P$  as the first derivative of enthalpy with respect to temperature. Comparison of eqs. (7) and (10) shows that both expressions are equivalent for  $dQ = \Delta Q/M$ , and the isobaric enthalpy change  $\Delta H$  is equal to the specific heat content  $\Delta Q/M$ .

Isobaric and isochoric specific heat capacity are related to compressibility  $\beta = \Delta V / (V \Delta P)$  and its inverse, incompressibility or bulk modulus  $K = V \Delta P / \Delta V$ , by  $c_P / c_V = \beta_T / \beta_S = K_S / K_T$  (e. g. Stacey & Davis, 2008) where subscripts T and S refer to isothermal and adiabatic conditions, respectively. Inserting the thermodynamic relation  $\beta_T = \beta_S + \alpha^2 T / (\rho c_P)$  (e. g. Birch, 1966) between isothermal and adiabatic compressibility yields the relative difference between isobaric and isochoric specific heat capacity:

$$c_P / c_V = 1 + \alpha \gamma T, \quad (11)$$

where  $\alpha = \Delta V / (V \Delta T)$  is the volume expansion coefficient,

$$\gamma = \frac{\alpha K_S}{\rho c_P} = \frac{\alpha K_T}{\rho c_V}, \quad (12)$$

the dimensionless Grüneisen parameter, and  $\rho$  density. Inserting the expressions for  $\alpha$  and  $K$  into eq. (12) yields:

$$\gamma = \frac{1}{\rho c_P} \frac{\Delta V}{V \Delta T} \frac{V \Delta P}{\Delta V} = \frac{\Delta P}{\rho c_P \Delta T}. \quad (13)$$

Thus the Grüneisen parameter  $\gamma$  is the relative pressure change in a material heated at constant volume.

For solids, i. e.  $f = 6$ , the absolute difference between isobaric and isochoric specific heat capacity follows from eqs. (11) and (8):

$$c_P - c_V = \frac{K_T \alpha^2 T}{\rho} = \frac{3 K_S \alpha^2 T}{4 \rho}. \quad (14)$$

For crustal rocks ( $\gamma = 0.5$ ;  $\alpha = 20 \mu\text{K}^{-1}$ ;  $T < 10^3 \text{ K}$ ;  $\rho = 2600 \text{ kg m}^{-3}$ ;  $K_S < 75 \text{ GPa}$  (Dziewonski & Anderson, 1981; Stacey & Davis, 2008), the difference between isobaric and isochoric specific heat capacity is less than  $9 \text{ J kg}^{-1} \text{ K}^{-1}$  or 1 % according to eqs. (14) and (11), respectively. Thus, the distinction between isobaric and isochoric specific heat capacity is negligible for crustal rocks at temperatures below 1000 K. However, it need be made for mantle rocks. From here on, “specific heat capacity” will always refer to isobaric specific heat capacity, denoted simply by the letter  $c$  without the subscript “P”.

This classical treatment of heat capacity is sufficient for temperatures above the Debye temperature. In the Earth, temperature exceeds the Debye temperature everywhere except in the crust (Stacey & Davis, 2008). Therefore, in experiments at room temperature and atmospheric pressure, we observe deviations from the values predicted by eqs. (3) – (14) which are based on classical Dulong-Petit theory. The lower the temperature, lighter the element, and stronger the lattice bonding become, the larger are these deviations.

Clearly, interpretation of heat capacity below the Debye temperature is beyond classical mechanics and requires quantum mechanical treatment. This is, however, beyond the scope of this text and interested readers are referred to standard physics textbooks (e. g. Tipler & Mosca, 2007). Therefore heat capacity at crustal temperatures should not be calculated from eqs. (3) and (14) but rather be measured or calculated from appropriate, quantum mechanical equations.

Čermák & Rybach (1982) compiled data on isobaric specific heat capacity for different rock forming minerals and different igneous, metamorphic, volcanic, and sedimentary rocks as well as the corresponding variations with temperature.

### Measuring techniques

Specific heat capacity  $c$  can be measured directly or derived as the isobaric derivative of enthalpy  $H$  with respect to temperature. Specific heat capacity of rocks varies with temperature, pressure, porosity, and saturants. Accordingly, in situ values may deviate from laboratory data according to temperature, pressure, and type and content of pore fluid.

Numerous steady-state and transient calorimetric methods are available for measuring specific heat capacity. The most popular are mixing or drop calorimeters and heat flux differential scanning (DSC) calorimeters. The first method yields an absolute value, the second one is a comparative method. All of these methods and their details are discussed in the literature (e. g. Hemminger & Cammenga, 1989; Brown, 2001; Haines, 2002) to which interested readers are referred. The isobaric enthalpy change (or specific heat content)  $\Delta H$  of solids may be determined by the method of mixtures using a Bunsen-type calorimeter in which the unknown isobaric enthalpy change of a sample relative to a base temperature, e. g. 25 °C, is compared to the corresponding known isobaric enthalpy change of platinum (Kelley, 1960; Somerton, 1992).

### Calculated heat capacity

When no direct measurements can be performed, isobaric enthalpy change and specific heat capacity of rocks can be calculated according to Kopp's law, eq. (15), as the arithmetic mean of the individual mineralogical and fluid contributions weighted by the volume fractions  $n_i$  of the  $N$  individual phases relative to total rock volume:

$$\Delta H = \sum_{i=1}^N n_i \Delta H_i; \quad c = \sum_{i=1}^N n_i c_i; \quad 1 = \sum_{i=1}^N n_i. \quad (15)$$

Based on data for various minerals (e. g. Kelley, 1960; Berman & Brown, 1985; Somerton, 1992; Waples & Waples, 2004), the isobaric enthalpy change  $\Delta H$  or specific heat capacity  $c$  can be computed from eq. (15) for any rock consisting of an arbitrary number of minerals with given volume fractions.

### Temperature dependence

Derived from measured variation of isobaric enthalpy change  $\Delta H$  with temperature of various oxides, Kelley (1960) suggested a second order polynomial for fitting  $\Delta H$  from which  $c_p = (\partial H / \partial T)_p$  can be easily calculated. Somerton (1992) and Clauser (2006) report  $\Delta H$  and  $c$  values of various rock forming oxides and pore fluids. An alternative approach is fitting heat ca-

capacity measured at different temperatures directly to polynomials of various degrees (e. g. Maier & Kelley, 1932; Berman & Brown, 1985; Fei & Saxena, 1987; Holland & Powell, 1996; Robertson & Hemingway, 1995). Waples & Waples (2004) provide a discussion of the various approaches. The polynomial proposed by Berman & Brown (1985),

$$C_{P,\text{mol}} = k_0 + k_1 T^{-0.5} + k_2 T^{-2} + k_3 T^{-3} \quad (T \text{ in K}), \quad (16)$$

works over a large temperature range and yields no values incompatible with the Dulong-Petit law for high temperatures. Tab. 2 lists values for the coefficients  $k_0 - k_3$  in eq. (16) determined from fits of heat capacity of selected minerals measured at different temperatures

**Tab. 2 Coefficients for calculating isobaric molar heat capacity  $C_{P,\text{mol}}$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) from eq. (16) (Berman, 1988).**

Mineral	Chemical Composition	$k_0$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )	$k_1 \times 10^{-2}$ ( $\text{J mol}^{-1} \text{K}^{-1/2}$ )	$k_2 \times 10^{-5}$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )	$k_3 \times 10^{-7}$ ( $\text{J mol}^{-1} \text{K}^{-2}$ )	T (K)
<i>Albite</i>	$\text{NaAlSi}_3\text{O}_8$	393.64	-24.155	-78.928	107.064	250 – 1373
<i>Almandine</i>	$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	573.96	-14.831	-292.920	502.208	420 – 997
<i>Andalusite</i>	$\text{Al}_2\text{SiO}_3$	236.48	-11.029	-75.268	93.644	254 – 1601
<i>Anorthite</i>	$\text{CaAl}_2\text{Si}_2\text{O}_8$	439.37	-37.341	0.0	31.702	292 – 1373
<i>Calcite</i>	$\text{CaCO}_3$	178.19	-16.577	-4.827	16.660	257 – 1200
<i>Cordierite</i>	$\text{Mg}_2\text{Al}_4\text{Si}_3\text{O}_{18}$	954.39	-79.623	-21.173	-37.021	256 – 1652
<i>Corundum</i>	$\text{Al}_2\text{O}_3$	155.02	-8.284	-38.614	40.908	250 – 2300
<i>Dolomite</i>	$\text{CaMg}(\text{CO}_3)_2$	328.48	-25.544	-46.885	79.038	250 – 650
<i>Enstatite (ortho)</i>	$\text{MgSiO}_3$	166.58	-12.066	-22.706	27.915	254 – 1273
<i>Fayalite</i>	$\text{Fe}_2\text{SiO}_4$	248.93	-19.239	0.0	-13.910	255 – 1370
<i>Forsterite</i>	$\text{Mg}_2\text{SiO}_4$	238.64	-20.013	0.0	-11.624	253 – 1807
<i>Hematite</i>	$\text{Fe}_2\text{O}_3$	146.86	0.0	-55.768	52.563	258 – 1757
<i>Kaolinite</i>	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	523.23	-44.267	-22.443	9.231	256 – 560
<i>Kyanite</i>	$\text{Al}_2\text{SiO}_3$	262.68	-20.014	-19.997	-6.318	252 – 1503
<i>Lime</i>	$\text{CaO}$	58.79	-1.339	-11.471	10.298	250 – 1176
<i>Magnesite</i>	$\text{MgCO}_3$	162.30	-11.093	-48.826	87.466	288 – 750
<i>Magnetite</i>	$\text{Fe}_3\text{O}_4$	207.93	0.0	-72.433	66.436	257 – 1825
<i>Muscovite</i>	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	651.49	-38.732	-185.232	274.247	257 – 967
<i>Periclase</i>	$\text{MgO}$	61.11	-2.962	-6.212	0.584	250 – 1798
<i>Potassium feldspar</i>	$\text{KAlSi}_3\text{O}_8$	381.37	-19.411	-120.373	183.643	250 – 997
<i>Quartz</i>	$\text{SiO}_2$	80.01	-2.403	-35.467	49.157	250 – 1676
<i>Sillimanite</i>	$\text{Al}_2\text{SiO}_5$	256.73	-18.827	29.774	25.096	253 – 1496
<i>Sphene</i>	$\text{CaTiSiO}_5$	234.62	-10.403	-51.183	59.146	255 – 1495
<i>Spinel</i>	$\text{MgAl}_2\text{O}_4$	235.90	-17.666	-17.104	4.062	256 – 1805
<i>Talc</i>	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	664.11	-51.872	-21.472	-32.737	250 – 639
<i>Wollastonite</i>	$\text{CaSiO}_3$	149.07	-6.903	-36.593	48.435	251 – 1433

As an alternative, Waples & Waples (2004) propose a statistical approach describing the general temperature dependence of all rocks and minerals which can be rescaled easily for individual rocks and minerals. To this end, measured specific heat capacity  $c_P$  was normalized by the corresponding normalizing value  $c_{P,n}$  at 200 °C (473.15 K), a temperature at or near which data was available. The resulting polynomial regressions yielded much better coefficients of determination  $R^2$  for data measured on non-porous rock ( $R^2 = 0.93$ ) than for those measured on minerals ( $R^2 = 0.62$ ) while the trends were similar. The regression on the combined data for minerals and non-porous rocks yields an expression for the normalized specific heat capacity of a mineral or non-porous rock at arbitrary temperature  $T$  with a coefficient of determination  $R^2 = 0.65$ :

$$c_{P,n}(T) = 0.716 + 1.72 \times 10^{-3} T - 2.13 \times 10^{-6} T^2 + 8.95 \times 10^{-10} T^3, \quad (T \text{ in } ^\circ\text{C}). \quad (17)$$

Equation (17) can be rescaled for any mineral or non-porous rock at any temperature  $T_2$  provided a value  $C_P(T_1)$  measured at temperature  $T_1$  is available, for instance from any of the

compilations of Berman & Brown (1985), Fei & Saxena (1987), Berman (1988), Holland & Powell (1996), or Robertson & Hemingway (1995):

$$c_p(T_2) = c_p(T_1) \frac{c_{p,n}(T_2)}{c_{p,n}(T_1)}. \quad (18)$$

Additionally, Waples & Waples (2004) consider the variation of specific heat capacity with lithology where interested readers find a specific discussion regarding coals of different carbon content or maturity.

Mottaghy et al. (2005) used a second-order polynomial in temperature to fit the variation of isobaric specific heat capacity with temperature measured on a suite of meta-sedimentary, volcanic, magmatic, and metamorphic rocks:

$$c_p(T) = A_0 + A_1 T^1 + A_2 T^2 \quad (c_p \text{ in J kg}^{-1} \text{ K}^{-1}, \quad 1^\circ\text{C} \leq T \leq 100^\circ\text{C}). \quad (19)$$

The average values for the coefficients  $A_0 - A_2$  determined from a regression of  $c_p(T)$  measured over a temperature range of  $1^\circ\text{C} - 100^\circ\text{C}$  on 26 samples from seven boreholes are:  $\bar{A}_0 = 747.17725 \text{ J kg}^{-1} \text{ K}^{-1}$ ;  $\bar{A}_1 = 1.862585346 \text{ J kg}^{-1} \text{ K}^{-2}$ ;  $\bar{A}_2 = -0.002510632231 \text{ J kg}^{-1} \text{ K}^{-3}$ .

Based on a composition of 30 % quartz, 60 % feldspar (albite), and 10 % phyllosilicates (5 % phlogopite, and 5 % annite), Whittington et al. (2009) suggest average “bulk crustal” molar specific heat capacity equations based on end-member mineral data for two temperature ranges, separated by the transition at 846 K ( $\sim 573^\circ\text{C}$ ) between  $\alpha$ - and  $\beta$ -quartz:

$$C_{p,\text{mol}}(T) = \begin{cases} 199.50 + 0.0857T - 5.0 \times 10^{-6} T^2 & ; T \leq 846 \text{ K} \\ 229.32 + 0.0323T - 47.9 \times 10^{-6} T^2 & ; T > 846 \text{ K} \end{cases}; \quad (C_{p,\text{mol}} \text{ in J mol}^{-1} \text{ K}^{-1}). \quad (20)$$

Assuming an average molar mass of  $0.22178 \text{ kg mol}^{-1}$  this yields the variation of isobaric specific heat capacity  $c_p$  with temperature shown in Fig. 1.

*Fig 1 goes here*

**Fig. 1 Variation of specific heat capacity  $c_p$ , the phonon components of thermal diffusivity and thermal conductivity  $\kappa_p$  and  $\lambda_p$ , respectively, and thermal capacity  $\rho c_p = \lambda_p/\kappa_p$  with temperature in an average crust according to eq. (20).**

### Volumetric heat capacity - thermal capacity

When heat capacity is related to unit volume rather than to unit mass or unit amount of substance it is referred to as volumetric heat capacity or thermal capacity. It can be calculated as the product of specific heat capacity  $c$  and density  $\rho$  or as the ratio of thermal conductivity  $\lambda$  and thermal diffusivity  $\kappa$  by

$$\rho c = \lambda / \kappa. \quad (21)$$

Again, Kopp’s law yields the rock’s bulk thermal capacity  $(\rho c)_b$  as:

$$(\rho c)_b = (1 - \phi)(\rho c)_s + \phi \sum_{i=1}^N S_i (\rho c)_i, \quad (22)$$

where  $\phi$  is porosity,  $(\rho c)_s$  thermal capacity of the rock skeleton,  $S_i$  fractional saturation, and  $(\rho c)_i$  thermal capacity of the  $i^{\text{th}}$  fluid phase in the pore space. The skeleton thermal capacity itself may be calculated again from Kopp’s law for a given mineral assemblage and the corresponding volume fractions of the solid phase from eq. (15). Because of the low density of air



and gas – about three orders of magnitude lower than that of water and rock – the contribution of the gas phase to thermal capacity can often be ignored. In this case,  $N = 2$  for the fluid phases water and oil or  $N = 1$  for water only. Expressions for the density of various fluids are reported in Clauser (2006). Data on density of various minerals and rocks are listed e. g. in Wohlenberg (1982a,b) or Olhoeft & Johnson (1989). Using eqs. (17) and (18), Waples & Waples (2004) analyzed a substantial collection of density and specific heat capacity data from various authors and transformed specific heat capacity and thermal capacity to a uniform reference temperature of 20 °C (Tab. 3).

**Tab. 3 Typical values or ranges for density  $\rho$ , isobaric specific heat capacity  $c_p$ , and thermal capacity  $\rho c_p$  of selected rocks at 20 °C (Waples & Waples, 2004; Petrunin et al., 2004).**

Rock	$\rho$ (kg m <sup>-3</sup> )	$c_p$ (J kg <sup>-1</sup> K <sup>-1</sup> )	$\rho c_p$ (kJ m <sup>-3</sup> K <sup>-1</sup> )
<i>albite</i>	2 540 – 2 560	755 – 780	1 922 – 1 991
<i>amphibole</i>	3 010	700 – 1 134	2 110 – 3 410
<i>anhydrite</i>	2 950 – 2 960	590 – 940	1 740 – 2 780
<i>anorthite</i>	2 740	800	2 202
<i>basalt</i>	2 870	880 – 900	2 526 – 2 583
<i>clay</i>	2 680	860	2 300
<i>coal</i>	1 350	1 300	1 760
<i>diabase</i>	2 790	731 – 860	2 040 – 2 400
<i>dolomite</i>	2 800	900	2 520
<i>gabbro</i>	2 970 – 3 000	650 – 1 000	1 950 – 2 970
<i>gneiss</i>	2 700	770 – 979	2 080 – 2 640
<i>granite</i>	2 620 – 2 650	600 – 1 172	1 590 – 3 070
<i>gypsum</i>	2 370	1 010	2 390

Rock	$\rho$ (kg m <sup>-3</sup> )	$c_p$ (J kg <sup>-1</sup> K <sup>-1</sup> )	$\rho c_p$ (kJ m <sup>-3</sup> K <sup>-1</sup> )
<i>limestone</i>	2 760 – 2 770	680 – 880	1 880 – 2 430
<i>peridotite</i>	2 740 – 3 190	705 – 1 005	1 930 – 3 210
<i>pyroxenite</i>	3 190 – 3 240	660 – 1 000	2 140 – 3 190
<i>quartzite</i>	2 640	731 – 1 013	1 930 – 2 670
<i>rock salt</i>	2 160	880	1 900
<i>sandstone</i>	2 640	775	2 050
<i>schist</i>	2 770 – 2 900	790 – 1 096	2 190 – 3 180
<i>serpentinite</i>	2 270 – 2 540	730 – 1 005	1 660 – 2 550
<i>siltstone</i>	2 680	910	2 449
<i>slate</i>	2 770 – 2 780	740 – 1 113	2 060 – 3 080
<i>syenite</i>	2 820	460	1 300
<i>talc</i>	2 780	1 000	2 780
<i>tuff</i>	2 750	1 090	3 000

The mean thermal capacity of “impervious” rocks was found at 2.300(46) MJ m<sup>-3</sup> K<sup>-1</sup> by Roy et al. (1981). This is acceptably close to the mean of 2.460(65) MJ m<sup>-3</sup> K<sup>-1</sup> found by Waples & Waples (2004) for inorganic minerals.

Based on density, specific heat capacity, and thermal conductivity measured at room temperature Mottaghy et al. (2005) determined thermal capacity as inverse slope of a regression of diffusivity on thermal conductivity according to eq. (21). All values fell well within  $\pm 20$  % of the average of 2.3 MJ m<sup>-3</sup> K<sup>-1</sup> recommended by Beck (1988).

Mottaghy et al. (2008) determined average values for thermal capacity according to eq. (21) for metamorphic and magmatic crystalline rocks as the inverse slope of a linear regression of values of thermal diffusivity versus thermal conductivity measured at temperatures in the range 20 °C – 300 °C:

$$\kappa(T) = \frac{\lambda(T)}{m + nT}, \quad (T \text{ in } ^\circ\text{C}), \quad (23)$$

Regression of data measured on seven samples collected along a profile crossing the Eastern Alps from north to south and on nine samples from the northern rim of the Fennoscandian Shield near the Kola ultra-deep borehole SG-3 yielded  $m = 2\,066(70) \text{ kJ m}^{-3} \text{ K}^{-1}$ ,  $n = 2.2(4) \text{ kJ m}^{-3} \text{ K}^{-2}$ ,  $R^2 = 0.97$  and  $m = 2\,404(91) \text{ kJ m}^{-3} \text{ K}^{-1}$ ,  $n = 3.6(5) \text{ kJ m}^{-3} \text{ K}^{-2}$ ,  $R^2 = 0.92$ , respectively. This yields a range of thermal capacity for the Alpine and Fennoscandian data of about 2.1 MJ m<sup>-3</sup> K<sup>-1</sup> – 2.7 MJ m<sup>-3</sup> K<sup>-1</sup> and 2.4 MJ m<sup>-3</sup> K<sup>-1</sup> – 3.5 MJ m<sup>-3</sup> K<sup>-1</sup>, respectively in the temperature range 20 °C – 300 °C.

The product of an average density of  $2700 \text{ kg m}^{-3}$  for the crust and isobaric specific heat capacity calculated for an average molar mass of  $0.22178 \text{ kg mol}^{-1}$  according to eq. (20) (Whittington et al., 2009) yields the variation of thermal capacity  $\rho c_p$  (eq. (21)) with temperature shown in Fig. 1. Its increase with temperature by about a factor of 1.7 in a temperature interval of 1000 K demonstrates that the effect of temperature is stronger for the phonon component of thermal diffusivity  $\kappa$  than for phonon thermal conductivity  $\lambda_p$  due to the increase of specific heat capacity. Assuming a constant density throughout the crust implies that the increase and decrease in density due to the increase in pressure and temperature, respectively, partly cancel each other and that these changes are small compared to those of specific heat capacity and thermal diffusivity.

## Latent heat

Solidification of magma and melting of rocks as well as freezing and thawing of water in soils or rocks liberates or consumes heat, respectively. The like applies to mineral phase changes such as those associated with the seismic discontinuities at 410 km, 520 km and 660 km in the transition zone from 410 km – 600 km between the upper and lower mantle. These mineral phases are chemically identical but differ with respect to crystal structure and therefore elastic properties. This is why this transition is seen in the seismic wave field. Phase transitions require a certain pressure  $P$  and temperature  $T$ , but also a specific relation between these two state variables expressed by the so-called Clapeyron slope  $dP/dT = \Delta S(P,T)/\Delta V(P,T)$  (the inverse of the Clausius-Clapeyron equation) where  $S$  and  $V$  are entropy and volume, respectively. This means that the depth where a certain phase transition occurs varies with the ambient temperature in the crust. Positive and negative values for the Clapeyron slope are associated with exothermic and endothermic reactions, respectively.

**Tab. 4 Comparison of isobaric specific heat capacity  $c_p$  and latent heat of melting  $L$  of granite, basalt, sea and fresh water (Stacey & Davis, 2008, supplemented).**

	granite	basalt	sea water	fresh water	dry air (15 °C, 1 atm)
$c_p \text{ (kJ kg}^{-1} \text{ K}^{-1})$	0.83	0.88	3.99	4.18	1.006
$L \text{ (kJ kg}^{-1})$	420	420	335	333.55	196

Phase changes generally consume or deliver much more latent heat than can be stored or delivered as sensibly heat: It requires a temperature increase of more than 500 K to equal by sensible heat the amount of latent heat required to melt 1 kg of granite and still an increase of more than 80 K to equal by sensible heat the amount of latent heat required to melt 1 kg of sea ice (Tab. 4).

The *discontinuity at 410 km* is generally associated with the transition in olivine from  $\alpha$ -olivine to  $\beta$ -spinel, also named wadsleyite (e. g. Stacey & Davis, 2008)). At expected pressure and temperature of 14 GPa and 1,600 K, respectively, corresponding values for the Clapeyron slope vary between  $2.9 \text{ MPa K}^{-1}$  –  $4.8 \text{ MPa K}^{-1}$  (Bina & Helffrich, 1994; Katsura et al., 2004, Stacey & Davis, 2008). The *discontinuity at 520 km* is associated with the transition from  $\beta$ -spinel (wadsleyite) into  $\gamma$ -spinel, also named ringwoodite (e. g. Stacey & Davis, 2008). At an expected pressure of 18 GPa a temperature increase, such as by an ascending plume, would require a higher pressure for this transition according to inferred Clapeyron slopes of  $4.0 \text{ MPa K}^{-1}$  –  $5.3 \text{ MPa K}^{-1}$  (Helffrich, 2000; Deuss & Woodhouse, 2001). A second transition occurs between garnet and calcium-perovskite ( $\text{CaSiO}_3$ ) where the iron in garnet goes into Ilmenite and its  $\text{CaSiO}_3$ -component into calcium-perovskite. This reaction has a negative Clapeyron slope. The two slopes of different sign may shift the depth for two transitions into opposite di-

reactions which is observed as a splitting of the 520 km discontinuity. The *discontinuity at 660 km* defines the transition into the lower mantle. It is caused by the transition of  $\gamma$ -spinel (ringwoodite) into magnesium-perovskite ( $\text{MgSiO}_3$ ) and ferrous periclase (magnesiowüstite,  $(\text{Fe,Mg})\text{O}$ ). At an expected pressure of 23.5 MPa this endothermic transition is associated with a Clapeyron slope of  $-2.8 \text{ MPa K}^{-1}$  (Stacey & Davis, 2008).

The latent heat  $L$  which corresponds to these additional heat sources and sinks can be elegantly combined with the specific sensible heat capacities of the liquid and solid rock,  $c_l$  and  $c_s$  respectively, into an effective bulk specific heat capacity  $c_{\text{eff}}$ . This effective specific heat capacity then accounts for the entire enthalpy change, including latent heat. In this approach, the latent heat effects are assumed to occur between the solidus and liquidus temperatures  $T_1$  and  $T_2$ , respectively. The heat liberated by a solidifying (“freezing”) liquid phase is obtained by weighting by the volume fractions of liquid and solid phases,  $\phi_l$  and  $\phi_s$ , respectively. The enthalpy change of the rock volume then becomes  $dH_{\text{freezing}} = (\phi_l c_l + \phi_s c_s) dT + L d\phi_l$ , and the effective heat capacity  $c_{\text{eff}}$  is:

$$c_{\text{eff}}^{\text{freezing}} = \frac{dH}{dT} = \phi_l c_l + \phi_s c_s + L \frac{d\phi_l}{dT}. \quad (24)$$

Conversely, when considering melting the solid phase, the enthalpy change of the rock volume is  $dH_{\text{melting}} = (\phi_l c_l + \phi_s c_s) dT + L d\phi_s$ , and the effective heat capacity in this case  $c_{\text{eff}}$  is:

$$c_{\text{eff}}^{\text{melting}} = \frac{dH}{dT} = \phi_l c_l + \phi_s c_s + L \frac{d\phi_s}{dT}. \quad (25)$$

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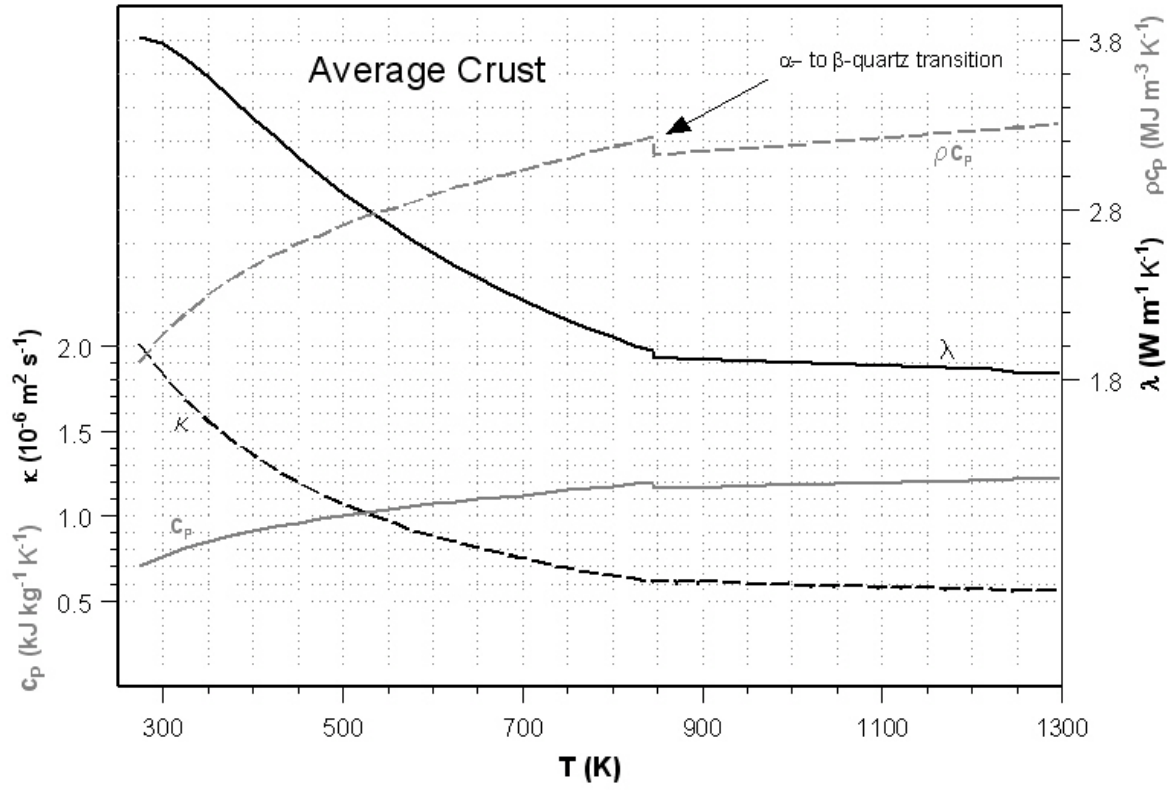
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## Cross-references

Thermal Storage and Transport Properties of Rocks, 2: Thermal conductivity and diffusivity  
Heat flow (continental, oceanic)  
Geothermal record of climate change



**Fig. 1** Variation of specific heat capacity  $c_p$ , the phonon components of thermal diffusivity and thermal conductivity  $\kappa_p$  and  $\lambda_p$ , respectively, and thermal capacity  $\rho c_p = \lambda_p/\kappa_p$  with temperature in an average crust according to eq. (20).