Thermophysical properties of a volcanic rock material

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Presented at the 16th European Conference on Thermophysical Properties, Imperial College, London, England, 1 – 4 September 2002

Abstract. To simulate and predict the behaviour of a lava flow, it is essential to have a thorough knowledge of its thermophysical properties. Therefore, thermal conductivity, specific heat, and viscosity of volcanic rock material were determined in a wide temperature range. Especially, the properties of the molten material were investigated in detail. The material was taken from the Pietre-Cotte lava flow located on the isle of Vulcano, north of Sicily. The thermal conductivity of the material was determined in the temperature range 293 – 1623 K by the hot-wire method. Melting occurs above 1100 K. The specific heat was measured by differential scanning calorimetry between 347 and 1671 K. The viscosity of the lava melt was determined with a rotational viscometer HAAKE M5. The viscometer was enclosed in a high-temperature furnace optimised for the temperature range 1373 – 1598 K.

1 Introduction

In 2001, the eruption of Etna in Sicily demonstrated the urgent need for lava flow predictions in order to save lives and property. Another active volcano is on the isle of Vulcano, north of Sicily (de Astis et al 1991; Frazzetta and La Volpe 1991). The village Porto with 250 inhabitants is located below the main cone La Fossa. During the summer months, more than 10 000 tourists visit this attraction every day. In 1739, a lava flow called Pietre-Cotte stopped just short of the village Porto.

For the simulations, the properties of molten lava are of essential interest. The thermal conductivity, specific heat, and viscosity of volcanic rock material have to be known over a wide temperature range. These material properties represent the key parameters for the description of the emplacement processes of lava flows. Numerical simulations can be verified by using these data and the geometry of the respective flow. If simulations are calibrated in this way, predicting the flow behaviour and damage potential of future lava effusion processes becomes more feasible and thus enables hazard assessment.

To determine specific heat and viscosity, standard methods can be applied—a differential scanning calorimeter (DSC) and a rotating viscometer, respectively. On the other hand, experimental determination of thermal conductivity of molten lava is associated with problems. Lava is chemically aggressive, even with respect to noble metals in some cases. Murase and McBirney (1973) applied a stationary cylinder apparatus with a central heating element to investigate different rock melts up to 1773 K. The relative uncertainty in the thermal conductivity values was 15%. Snyder et al (1994) used the hot-wire method to determine the thermal conductivity of $CaMgSi_2O_6$ between 1673 and 1873 K. They used unprotected rhodium and iridium wires whose electric resistance had to be determined before each experimental run. The end effect, ie parasitic heat losses via the wire ends, was taken into account by performing successive experiments with a short and a long wire. The stated uncertainty is about 30%. The laser-flash technique

was also applied to estimate the thermal diffusivity $\alpha = \lambda/(\rho c_p)$, and thus with known values of density ρ and specific heat c_p, to derive the thermal conductivity λ (Büttner et al 1998). However, this method has the disadvantage that three properties have to be determined accurately to reach the given uncertainty below 9% and the experimental effort is large and expensive.

Data bases on the thermophysical properties of lava are very rare. As far as we know, no literature data on the thermal conductivity of rhyolite lava type are available. Murase and McBirney (1973) investigated the Newberry rhyolite obsidian which is mainly a clear black glass, which appears very different from the Pietre-Cotte lava, even though the chemical composition is similar. Stein and Spera (1998) determined the viscosity of rhyolite-vapour emulsions at magmatic temperatures by concentric-cylinder rheometry.

The aim of this work was to determine the specific heat, viscosity, and thermal conductivity of the Pietre-Cotte lava especially in the liquid phase, thus providing exact data for simulating lava flows.

2 Description of the Pietre-Cotte lava
The material was taken from the Pietre-Cotte lava flow located on the isle of Vulcano, north of Sicily. The lava mainly consists of 73.4 wt% SiO_2 and 13.4 wt% Al_2O_3 (de Astis et al 1997). Detailed analysis is given in table 1.

Table 1. Composition of the Pietre-Cotte lava (de Astis et al 1997). The composition is typical for a rhyolite stream with a characteristically high amount of SiO_2.

Compound	Content/wt%	Compound	Content/wt%	Compound	Content/wt%
SiO_2	73.43	FeO	1.67	Na_2O	4.07
TiO_2	0.11	MnO	0.07	K_2O	4.95
Al_2O_3	13.42	MgO	0.01	P_2O_5	0.02
Fe_2O_3	0.03	CaO	0.86	other	1.36

Before determining the thermophysical properties, the material needs to be homogenised and probable alteration due to hydration of glass must be reversed. Therefore the lava was crushed, mixed, and remelted in a furnace at 1473 K under buffered oxygen fugacity (iron – wustite-buffer). The homogenised, degassed, and molten material was then quenched in a water bath to form a granulate. This granulate was used for the further measurements.

3 Experimental methods
3.1 Thermal conductivity measurement
The thermal conductivity of the lava was determined by the hot-wire method (Ebert et al 1998). In principle, a thin wire is embedded in the sample. The wire is heated by a constant electric power and the increase of the electric resistance of the wire is recorded over time. The temperature values are calculated from the resistance. The thermal conductivity is derived from this time-dependent increase (Büttner et al 2000).

In this experiment, a 200 µm platinum – rhodium wire was used (see figure 1). The length of the wire was 71.1 mm. The wire was inserted in an Al_2O_3 tube with an outer diameter of 300 µm, which protected the wire from the chemically aggressive compounds of the lava sample. A detailed description of the preparation technique and the experimental set-up is given elsewhere (Ebert et al 1998).

The protective Al_2O_3 tube gives rise to an additional thermal contact resistance: the air gap between the wire and tube, both of which are very fragile. Nevertheless, the effect of this air gap on the measurement curve can be accounted for by using an appropriate
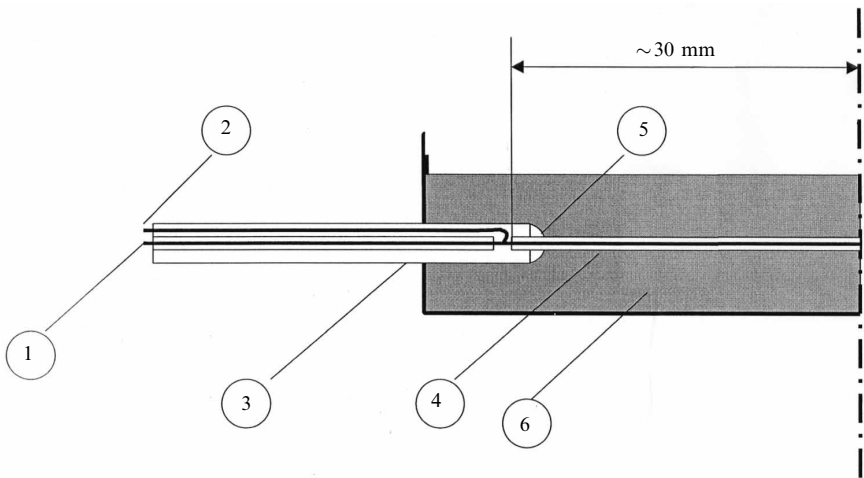
Figure 1. Schematic view (not true to scale) of the half hot-wire cell for determining the thermal conductivity of lava. The lava (6) is filled in an Al_2O_3 mould. The hot wire (1) with the potential wires (2) are encapsulated in Al_2O_3 tubes (3, 4). The open connections have to be sealed with Zr_2O_3 paste (5).

theoretical solution developed in our research group (Ebert et al 1993). The relative uncertainty (95% confidence interval) in the determined thermal conductivity values is 5%.

The ceramic mould was filled with the lava granulate, and the hot wire embedded. The mould was heated in a chamber furnace just above the melting point. Then the thermal conductivity measurements were performed up to the maximal temperature of 1623 K. The thermal conductivity was also determined during the cooling phase. Furthermore, a second run was executed, now starting at room temperature, up to 1473 K.

Figure 2 shows a typical temperature increase T_w of the hot wire at a temperature of 1473 K together with the fitted theoretical curve. At this temperature, the lava sample is already liquid. The experimental curve is closely described by the applied theoretical solution, which can be also seen in figure 3. Here, the percentage deviation of the experimentally derived temperature increase from the theoretically calculated temperature increase T_w is plotted, and is below 0.5% during the measurement time.
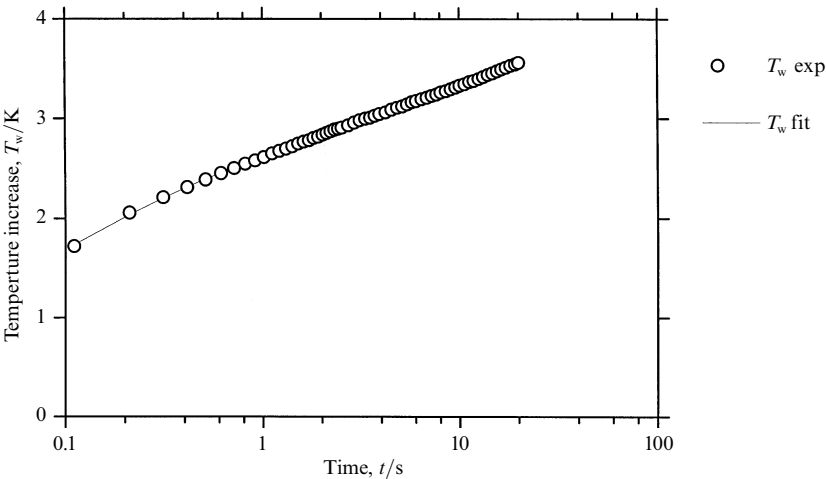

Figure 2. Typical measurement curve for a hot-wire measurement on liquid lava at 1473 K. Increase of the hot-wire temperature as a function of time: circles denote experimental data, line gives fit values.
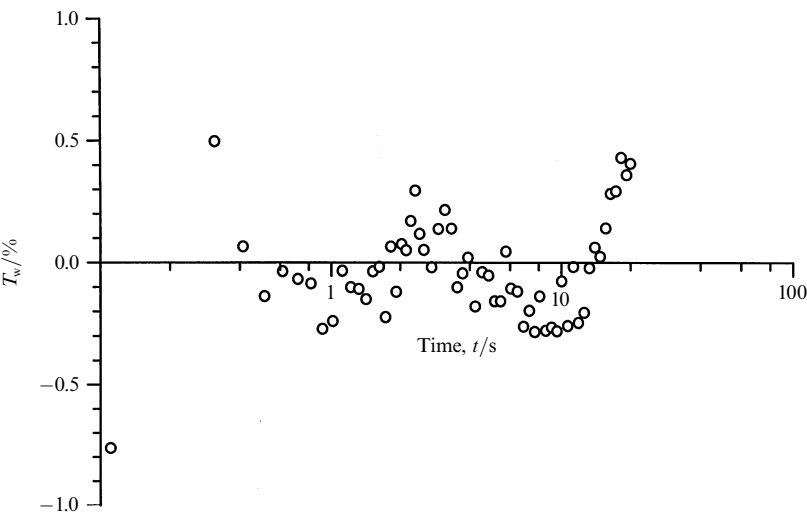
Figure 3. Percentage deviation, between the experimentally determined temperature increase and the theoretical fit values $(\lambda_{exp} - \lambda_{fit})/\lambda_{fit}$ for a hot-wire measurement on liquid lava at 1473 K.
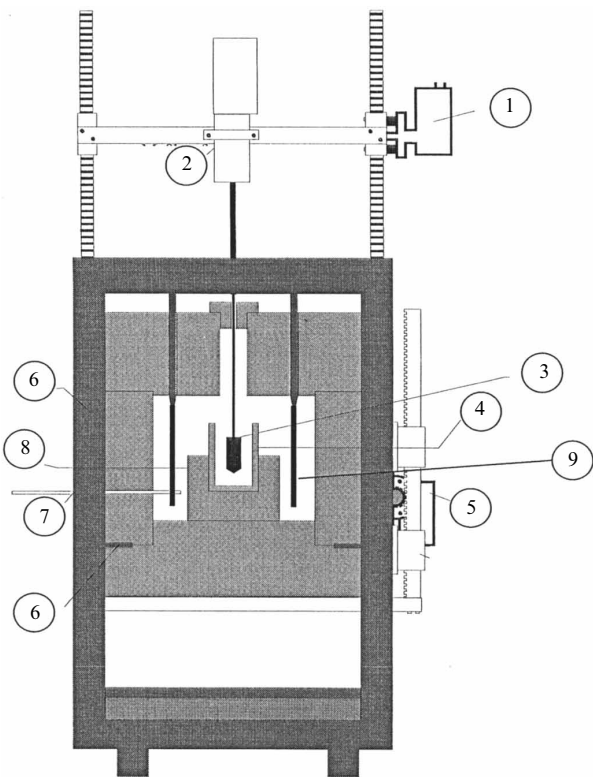

Figure 4. Schematic set-up of the rotational viscometer: (1) motor for withdrawing the measuring head, (2) measuring head, (3) rotating solid, (4) MgO crucible, (5) motor for withdrawing the furnace bottom, (6) steel construction, (7) gas inlet, (8) thermal insulation, and (9) heating element.

3.2 *Viscosity measurement*

To determine the viscosity, a commercial rotational viscometer of the type HAAKE M5 was used in combination with a specially designed furnace (see figure 4). The

relative temperature variation within the sample is less than 2 K at the maximum operational temperature of 1673 K. The relative uncertainty in the determination of the absolute temperature is less than 5%. All measurements were performed under a dynamic inert-gas atmosphere (95% argon, 5% nitrogen). The viscometer was calibrated with different silicone oils at room temperature and with Schott TV-glass type 8056 for temperatures above 1273 K. The relative uncertainty in the determined values of viscosity is below 8%.

3.3 *Specific heat measurement*

To determine the specific heat, the high-temperature DSC 404 (Netzsch-Gerätebau GmbH) was used. The measurements were performed under a dynamic argon atmosphere in the temperature range between 347 and 1671 K. In order to minimise the influence of thermal radiation on the DSC measurements, platinum crucibles with Al_2O_3 inlets were used. The sample mass was 22.75 mg. The DSC was calibrated against a sapphire standard. The granulate was heated to the maximum temperature and then cooled down—in both cases with a constant heating/cooling rate of 20 K min^{-1}. After this procedure, the molten lava was in good thermal contact with the crucible. Then the sample was heated a second time at the same heating rate of 20 K min^{-1}. From this run the specific heat was derived.

4 Results and discussion

The temperature dependence of the viscosity η can be described by the empirical equation (Murase and McBirney 1973):

$$\eta = \eta_0 \exp(E_\eta/RT) \ , \tag{1}$$

where η is viscosity, η_0 is a constant, E_η is activation energy, R is gas constant, and T is temperature. Figure 5 shows the viscosity as a function of temperature for two experimental runs in an Arrhenius diagram. The two curves are in good agreement. The activation energy is calculated at $\sim$295 kJ mol^{-1}.

In figure 6, the specific heat of the lava is shown as a function of temperature. The relative uncertainty is below 10%. Up to 1000 K, a typical increase in the specific heat with rising temperature can be observed. The c_p values are in the same range as determined for other types of lava (Büttner et al 1998). At 986 K an endothermal peak occurs. The exothermal peak between 1100 and 1200 K can be attributed to a structural
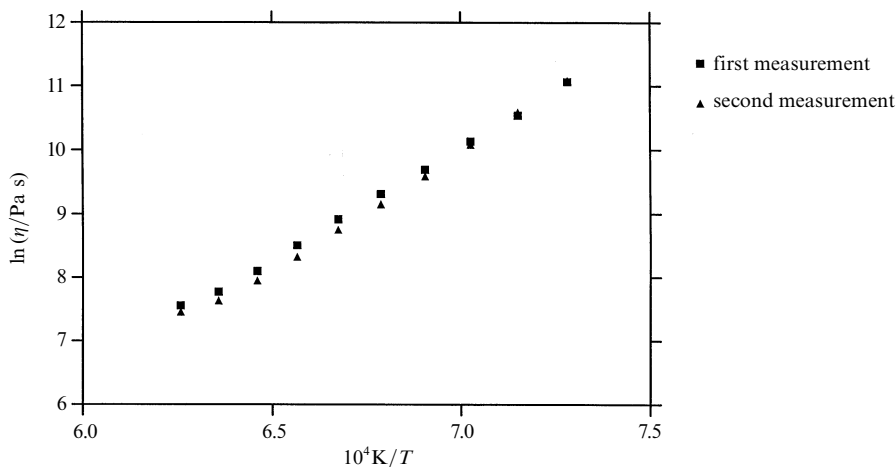

Figure 5. Arrhenius plot of the experimentally determined viscosity η of the Pietre-Cotte lava as a function of temperature T for two different experimental runs.
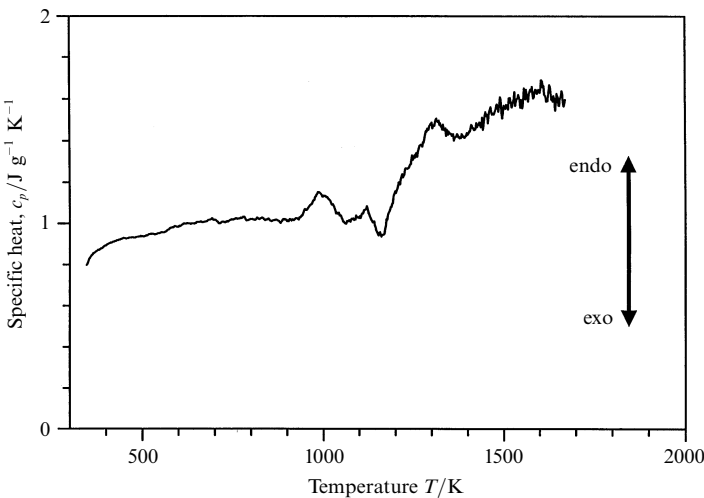
Figure 6. Experimentally determined apparent specific heat c_p of the Pietre-Cotte lava as a function of temperature T. Between 1000 and 1400 K different endothermal and exothermal peaks are superimposed on the specific heat.

relaxation (DeBolt et al 1976). The rise between 1100 K and 1400 K is caused by the transformation of the solid into a liquid. Above 1400 K the specific heat of the liquid lava increases again with temperature, but at a higher rate. The total heating enthalpy up to 1671 K is 1556 J g^{-1}. No mass loss during the measurement could be detected.

The experimentally determined values of thermal conductivity, λ, are plotted in figure 7. For $T < 1000$ K, the thermal conductivity increases with temperature as is expected for a glassy material with a very small phonon mean free path. Thus the increase is determined by the temperature-dependent specific heat. A small peak in the thermal conductivity can be observed at about 673 K. Above 1000 K, the thermal conductivity shows a maximum at about 1100 K. Above that temperature the values of λ decrease with temperature which corresponds to the melting of the lava. At 1623 K the curves show a
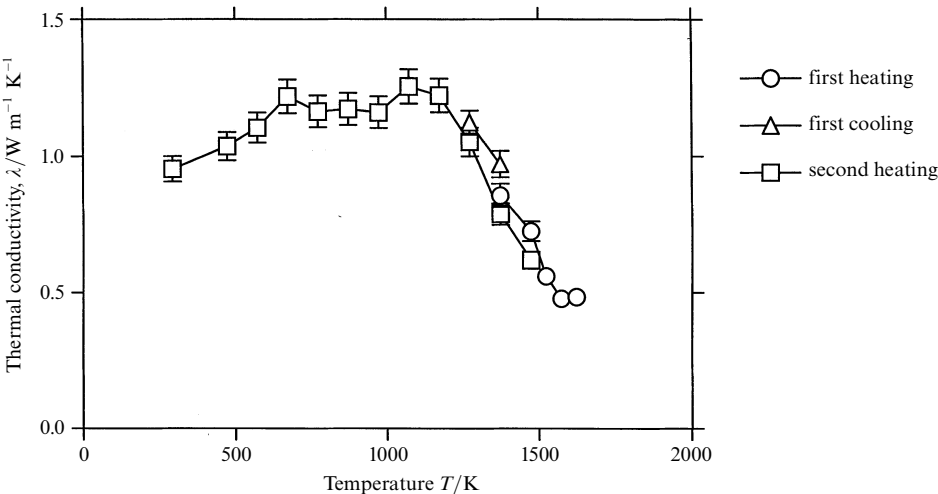

Figure 7. Experimentally determined values of the thermal conductivity of the Pietre-Cotte lava as a function of sample temperature. After the lava granulate was melted, the thermal conductivity of the liquid lava was measured up to 1623 K (first heating), two measurements were performed with decreasing temperature (first cooling) and a second experimental run was performed between ambient temperature and 1473 K (second heating).
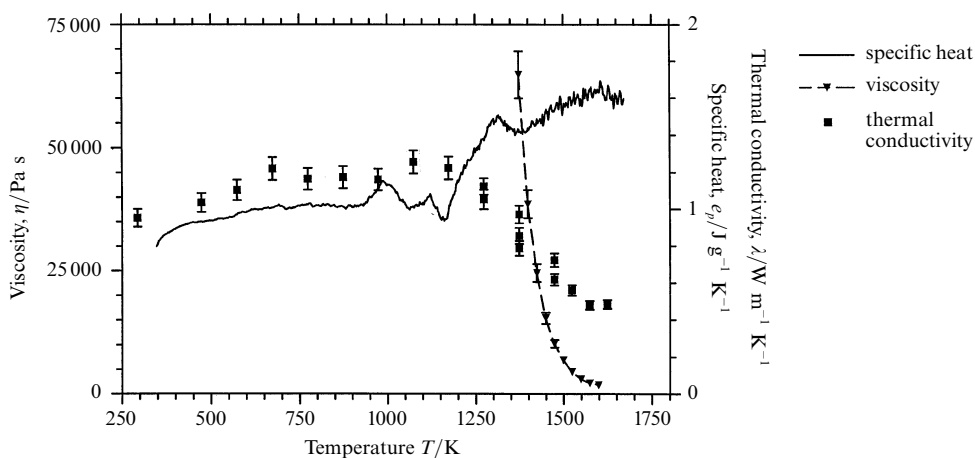
Figure 8. Compilation of the measured viscosity, specific heat, and thermal conductivity as a function of temperature. Between 1000 and 1400 K different endothermal and exothermal peaks are superimposed on the specific heat.

minimal λ of 0.48 W m^{-1} K^{-1} which indicates the end of the melting process. Within the melting zone, three single runs were performed. One during the first heating, the second during the first cooling process and, finally, the third during a second heating. At the beginning and at the end of the transition zone the data are in good agreement within the reported uncertainty interval. Some small differences between the thermal conductivity values of the three runs can be observed within this region which are within 10% and can be explained by the complex chemical and physical processes during the melting and solidifying process.

Figure 8 compiles the experimental values of the viscosity, specific heat, and thermal conductivity as a function of temperature. The thermal conductivity is seen to correlate closely with the specific heat up to 1150 K. The onset of the glass transition corresponds to a decrease in thermal conductivity. The upper end of the transition zone can be observed at $T = 1550$ K in all three properties.

5 Conclusion

In this paper, the values of viscosity, specific heat, and thermal conductivity of the Pietre-Cotte lava are presented in a wide temperature range for the first time. The specific heat was determined by conventional differential scanning calorimetry. The solid/liquid phase transition takes place in the temperature range 1100 – 1400 K and is characterised by a glass transition. The thermal conductivity was determined by the hot-wire method. The technique and evaluation method yield reliable values of the thermal conductivity. The relative uncertainty of the determined values is below 5%. The thermal conductivity ranges from about 1.3 W m^{-1} K^{-1} at $\sim$1100 K to about 0.5 W m^{-1} K^{-1} at $\sim$1620 K. The viscosity was determined in the temperature range 1370 – 1600 K varying from 65 000 Pa s down to $\sim$2000 Pa s. The thermophysical data determined here provide a reliable data base for simulations predicting the flow behaviour and the damage potential of future lava effusion processes, and are thus of vital use for hazard assessment.

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