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Effect of alkalis, phosphorus, and water on the surface tension of haplogranite melt

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ABSTRACT

The sessile drop method has been used for measurements of the surface tension of haplogranite (HPG) melts containing an excess of alkalis and phosphorous (HPG8, HPG8 + 5 wt% Li_2O, 5 wt% Na_2O, 20 wt% Na_2O, 5 wt% K_2O, 5 wt% Rb_2O, 5 wt% Cs_2O, 10 wt% P_2O_5) and of Armenian rhyolite in the temperature interval, 650–1665 °C, and at 1 bar pressure. Sessile drops were placed on graphite substrates in a Pyrox tube furnace purged with Ar. Drop shape was monitored with a videocamera and stored in a videorecorder. The surface tension was calculated by measuring the two principal radii of curvature of the drop shape in vertical cross section. The precision of the method was checked against the surface tension of water. The surface tension of HPG and rhyolite melt is ~280–300 ± 5 mN/m in the temperature interval 1200–1400 °C. Temperature dependence of the surface tension of haplogranite melts and rhyolite is weak and positive ($d\sigma/dT$ = 0.06 to 0.09 mN/m/°C). Addition of 5 wt% of alkali oxides (except Li_2O) results in a decrease of the surface tension of haplogranite melts. The HPG melts with 10 wt% P_2O_5 have 30% higher surface tension than haplogranite melts with excess alkalis, and a negative temperature derivative ($d\sigma/dT$ = –0.1 mN/m/°C). The HPG melts with 20 wt% Na_2O and 5 wt% Li_2O exhibit a decrease in surface tension with temperature ($d\sigma/dT$ = –0.02 and –0.10 mN/m/°C, respectively).

The surface tension of HPG8 melt saturated with water at 1–4 kbar was measured on sessile drops quenched at high pressure in an internally heated gas vessel at temperatures of 800–1200 °C. Water pressure significantly decreases the surface tension of melt from 270 mN/m at 1 bar (1000 °C) to 65 mN/m at 4 kbar. At 1 bar in "dry" conditions, $d\sigma/dT$ = +0.056 mN/m/°C and at 3 kbar of water pressure, $d\sigma/dT$ = +0.075 mN/m/°C. The decrease in the surface tension of HPG melt at a water pressure of several kbars is from –10 to –30 mN/m/wt% H_2O. The increase of water content to more than 10 wt% in granite melts may not result in any significant decrease in the surface tension, which may be explained by formation of a surface sublayer having physical properties very distinct from those of the bulk.

INTRODUCTION

The surface tension between magmatic melt and a saturating fluid phase is an important parameter influencing nucleation and growth of bubbles in natural magmas. During decompression and degassing of shallow magmas, the nucleated vapor phase expands, often contributing to the intensity of explosive volcanism. In order to estimate nucleation rates and critical sizes of vapor embryos, an experimental data base is needed for the surface tension between the silicate melt and a vapor phase (e.g., Bottinga and Javoy 1991; Hurwitz and Navon 1994). This is emphasized in volcanological applications of both homogeneous and heterogeneous nucleation theories where the surface tension between melt and gas is incorporated in the calculation of nucleation and bubble growth (Sparks 1978; Toramaru 1990; Lyachovsky et al. 1996). Crucial in these calculations is the influence of vapor phase on the physical properties of the surface between the melt and vapor. Furthermore, from rheology theories for soft inclusion suspensions, we know that the ratio of the viscous stress to surface tension (Capillary number = $D\dot{\varepsilon}\eta/\sigma$, where D is the size of a bubble, $\dot{\varepsilon}$ the strain rate of flow, η the shear viscosity, and σ the surface tension of the interface) characterizes the ability of bubbles to deform in a shear flow. Thus, knowledge of the surface tension provides input for the estimation of the time-dependent rheology of bubble-bearing magmas and rheological instabilities in viscous lava flows (Bagdassarov and Dingwell 1993b; Manga et al. 1998).

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BACKGROUND

The surface tension of natural silicate melts was studied at 1 bar by the detachment of right cylindrical bobs in melts of initially vitreous and crystalline basalts, Mount Hood andesite, and Samoa limburgite (Walker and Mullins 1981), and by the detachment of a Pt pin in the Di-An system (Taniguchi 1988). The sessile drop method was used to measure the surface tension of Columbia River basalt, Mount Hood andesite, a rhyolitic obsidian from Newberry crater, and a synthetic lunar sample (Murase and McBirney 1973). The temperature dependence of the surface tension reported in these studies varies significantly. Walker and Mullins (1981) reported a rather weak positive temperature dependence of all studied melts in the temperature interval 1200–1500 °C: σ = 360–350 mN/m, $d\sigma/dT$ = +0.03 ± 0.02 mN/m/°C. For pure diopside melt, the thermal coefficient of the surface tension is positive (+0.046 mN/m/°C); however, as the amount of the An component increased, the temperature dependence was shown to be strongly negative [–0.106 mN/m/°C for Di_{80} to –0.38 mN/m/°C for Di_{40} (Taniguchi 1988)]. In the study of Murase and McBirney (1973), the observed temperature dependence of the surface tension was 10 times larger (from +0.2 to +0.3 mN/m/°C) than in any other silicate melt. In general, aluminosilicates possess a rather weak positive temperature dependence of the surface tension [< +0.1 to +0.15 mN/m/°C (e.g., Weirauch and Ziegler 1996)]. The surface tension of silicate melts in general decreases with increasing silica content (Kozakevitch 1959). It may vary only from about 350 to 300 mN/m, if SiO_2 is greater than 65–75 wt% (King 1951; Popel and Esin 1957; Sharma and Philbrook 1970). The small increase in the surface tension with increasing content of basic oxides has been explained by the low surface tension of silica itself. In contrast, corresponding increases in shear viscosity or electrical conductivity of melt that accompany the addition of basic oxides to silica melt are much more significant (King 1951).

The surface tension of magmatic melts in the presence of volatiles is quite variable. The surface tension of basalt (quartz tholeiite) from Kamchatka was measured by Khitarov et al. (1979) both by a sessile drop method at 1 bar and from quenched sessile drops at water pressures up to 5 kbars. At 1 bar pressure, the temperature dependence of the surface tension is practically zero (< 0.01 mN/m/°C), which allowed these authors to use quenched sessile drops for estimation of the water pressure effect on the surface tension.

The effect of water on the surface tension turns out to be very significant. Under "dry" conditions (pressure of nitrogen), the surface tension of quartz tholeiite decreases from 400 mN/m at 1 bar and 1250 °C to 300 mN/m at 5 kbar. This effect also may be attributed to the dissolution of nitrogen gas in the surface layer. The magnitudes of the difference in gas solubility between bulk and surface concentrations might be significant. At 5 kbar water pressure, the surface tension of basaltic melt decreases to 90 mN/m (Khitarov et al. 1979). The authors know only one reported estimate of the surface tension of water-bearing granite melts (Epel'baum et al. 1973). The estimated surface tension of Rapakivi granite melt at 950 °C was 71 and 67 mN/m for 4.48 and 5.41 wt% of H_2O, respectively. For the system Qz-Ab-Or-H_2O, these authors reported values of the surface tension as low as 40–35 mN/m without noting any temperature dependence.

Few experimental studies have been conducted to assess the wetting angle between alkaline-bearing silicate melts and crystals at high temperatures. This is unfortunate because knowledge of this wetting angle would enable the choice of a suitable substrate for sessile drop studies. The wetting angle was measured between basaltic melt and different crystalline substrates by the use of the optical visualization of sessile drops (Khitarov et al. 1979), and between silicate melts containing Ca, Li, Na, or K and olivine crystals by the use of the interferometric technique (Wanamaker and Kohlstedt 1991). The purpose of the present study is to characterize the surface tension of haplogranite melts and the effect of excess alkalis and water using the experimental technique of a sessile drop at 1 bar and at water pressures up to 4 kbar applied earlier to basaltic melt (Khitarov et al. 1979).

EXPERIMENTAL METHOD

Experiments at 1 bar were conducted in a Pyrox-tube furnace purged with Ar gas. The gas was passed through the furnace at a flow rate of 50 cm^3/min. Inner diameter of the Al_2O_3-ceramic tube is 24 mm. The furnace has two flat optical windows made from quartz glass on both sides. Sessile drops were placed in the center of the furnace on substrates made from spectral quality graphite (RW405, SGL-Carbon, Germany). Substrates were machined in the form of discs 12 mm in diameter and 3 mm thick. Graphite is one of the materials providing a contact angle >90° with silicate melts. Sample glasses of haplogranitic compositions (see Table 1) were fused from mixtures of oxide powders by using a procedure described elsewhere (e.g., Knoche et al. 1992). Cylinders of glass 8 mm in diameter and 7–9 mm in height were drilled out from haplogranite glass batches. The weight of samples used in the sessile drop experiments ranged between 4.7–5.1 g. Samples of Armenian rhyolite were drilled directly from a cobble of the obsidian. Chemical compositions of samples were analyzed by solution-based ICP and electron microprobe methods. Details of procedures for chemical analysis were reported in previous publications (for haplogranitic glasses with an excess of alkalis, see Hess et al. 1995; for haplogranitic glasses with phosphorous, see Dingwell et al. 1993; for Armenian rhyolite, see Bagdassarov and Dingwell 1993a). Cylinders of glass were heated up to their melting temperatures at which they deformed to subspherical shapes. The shape of the sessile drops was monitored with a Sanyo VCC-2972 videocamera and stored on a Panasonic AG-67A-E videorecorder with programmed time-steps. The videocamera was aligned optically with the axis of the furnace by using a screen-mark and a pointer source of light directed from the opposite optical window. At temperatures above 950 °C, a sessile drop emits black-body radiation. To view the profile of a sessile drop a diffuse source of light was used from the opposite side of the videocamera optical window. Sessile drops were monitored with and without an optical filter. The differences in the observed drop dimensions were less than the uncertainty in the surface tension calculations. The video images of sessile drops obtained during the

TABLE 1. Chemical compositions of glasses

Oxide	Rhyolite (Armenia)	HPG8	HPG8 + 5 wt% Na_2O	HPG8+ 5 wt% Li_2O	HPG8 + 5 wt% K_2O	HPG8 + 5 wt% Rb_2O	HPG8+ 5 wt% Cs_2O	HPG8 + 20 wt% Na_2O	HPG8 + 10 wt% P_2O_5*
SiO_2	75.6 (0.6)	78.6 (0.4)	74.1 (0.4)	73.2 (0.3)	74.6 (0.8)	74.2 (0.7)	74.2 (1.3)	62.4 (0.4)	71.1 (0.3)
TiO_2	0.2 (0.1)								
Al_2O_3	12.9 (0.3)	12.5 (0.2)	11.7 (0.6)	12.9 (0.3)	11.8 (0.8)	12.6 (0.4)	11.6 (0.7)	10.1 (0.3)	11.3 (0.2)
FeO†	0.9 (0.2)								
MnO	0.2 (0.1)								
MgO	0.2 (0.1)								
CaO	1.0 (0.1)								
Na_2O	4.1 (0.7)	4.6 (0.3)	9.0 (0.2)	4.3 (0.3)	4.4 (0.8)		4.8 (0.4)	23.5 (0.2)	3.8 (0.4)
K_2O	4.6 (0.5)	4.2 (0.2)	4.4 (0.9)	4.4 (0.2)	9.2 (1.0)	4.3 (0.2)	4.0 (1.0)	3.4 (0.2)	3.7 (0.4)
P_2O_5									9.5 (1.0)
Cs_2O							4.3 (1.0)		
Rb_2O						5.2 (0.9)			
Li_2O				4.9 (0.4)					
Total	99.7	99.9	99.2	99.7	100.0	101.1	98.4	99.4	99.4
ρ, g/cm^3	2.313	2.334	2.354	2.355	2.353	2.359	2.390	2.467	2.250
$\alpha \cdot 10^{-6}$/°C	25	33	56	70	59	43	44	99	27

Notes: Average of 8–10 ICP-AES analyses, numbers in brackets are standard deviations (Hess 1996). Density ρ at 22 °C was measured by the Archimedean double weighing method in air and toluene, coefficient of the thermal expansion α_v of these compositions was measured in a dilatometer (Knoche et al. 1995).

* Average of 10 microprobe analyses Cameca SX-50, 15 kV, 15 nA, 20 μm spot size, 20 s counting time.

† Total iron as FeO.

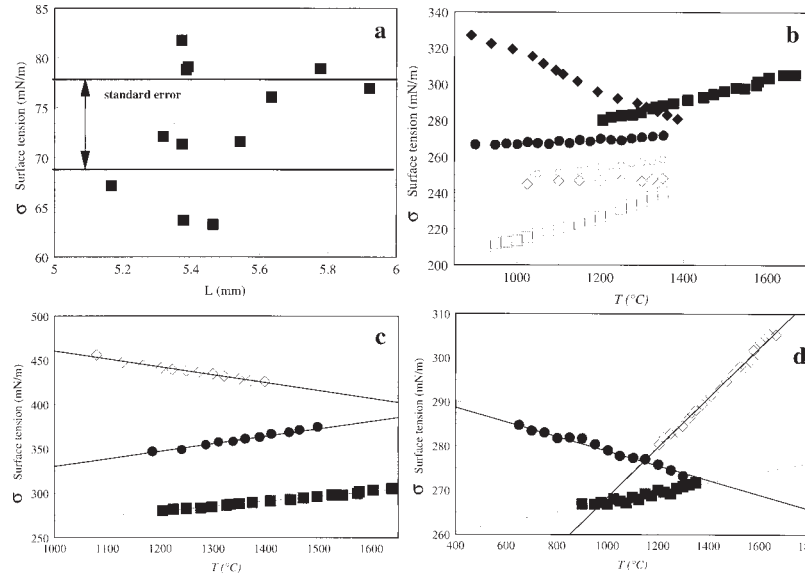

FIGURE 1. (**a**) Calibration of the sessile drop method at room temperature by using water drops of different sizes. A good agreement with the table value 72.8 mN/m at 20 °C can be achieved on sessile drops with the equatorial diameter about L ~5.5–6 mm. (**b**) The effect of 5 wt% of alkali oxides on the surface tension of HPG melt. Excess alkalis shifts the temperature interval of measurements due to the effect of alkalis on the glass transition temperature and viscosity (Hess et al. 1995). Closed large squares = HPG composition, closed diamonds = HPG + 5 wt% Li_2O, closed circles = HPG + 5 wt% Na_2O, open circles = HPG + 5 wt% Cs_2O, open diamonds = HPG + 5 wt% Rb_2O, open squares = HPG + 5 wt% K_2O. Error of surface tension measurement is about the size of large symbols. (**c**) HPG (closed large squares) and rhyolite melt (closed circles) have a similar positive slope of surface tension with temperature. Addition of 10 wt% of P_2O_5 to HPG melt (open diamonds) results in an increase of the surface tension and its negative slope with temperature. (**d**) The effect of 5 (closed large squares) and 20 wt% (closed circles) Na_2O on the surface tension of HPG melt (open diamonds). Addition of 20 wt% Na_2O provides quite different surface and bulk structural units in HPG melt.

run were stored in a PC and analyzed with the Image Processing Code (DIANa Bildanalyse). Gray images were converted into binary images and *x*-*z*-coordinates of the sessile drop profile were generated from the boundary pixels of a sessile drop image. The coordinates were scaled against a reference of known dimension with a precision ±0.001 mm. As a reference we used an Al_2O_3-plate (Al23, Frialit-Degussit, 14 mm in diameter) whose dimension was measured at room temperature and the thermal expansion coefficient is known. The *x*-*z*-coordinates of the drop profile were analyzed with the FORTRAN code described below.

To estimate an absolute error of the method, a calibration was done using sessile drops of distilled water at 22 °C. Sessile drops of different size were monitored and the surface tension from these experiments is compared with the table value in Figure 1A. It is important in using the sessile drop method to choose a proper drop size (Sangiorgi et al. 1982). If the initial volume of a drop is too large, the sessile drop breaks into several smaller droplets because the gravity effect is higher than the surface tension. If the size is too small, the error of the surface tension measurements is too high because the deformation of a drop from gravity may be negligible.

In the sessile drop method two parameters of the drops must be measured: horizontal equatorial diameter and vertical apex height. For the water drop, a horizontal diameter 5.5–5.9 mm provides an absolute experimental error of less than 6 mN/m (see Fig. 1A). The mean measured value of water surface tension at 22 °C is 73.4 mN/m, which is in satisfactory agreement with the reported value 72.8 mN/m at 20 °C (Weast et al. 1965). For experiments on silicate melts at high temperature, we estimate that the absolute error of the surface tension measurement is ±5 mN/m. The relative error, however, among measurements conducted on the same sessile drop at different temperatures does not exceed ±0.5 mN/m. This variation of surface tension is measurable by the sessile drop method.

The maximum size of the sessile drop was restricted by the inner diameter of the furnace and was chosen to optimize the deformation of the drop due to the force of gravity (Sangiorgi et al. 1982). Before measuring a drop profile, sessile drops of silicate melts must be kept at the desired constant temperature during a certain period of time depending on the shear viscosity of melt. This procedure is necessary to ensure relaxation of the drop shape. The time necessary to attain a relaxed sessile drop shape can be calculated as follows:

$$\tau_{relax} = \frac{D\eta}{\sigma} \quad (1)$$

where η is the shear viscosity, σ the surface tension, and D the diameter of a drop. The viscosities and densities of these haplogranite melts have been determined in separate experimental studies (Hess et al. 1995; Dingwell et al. 1993; Bagdassarov and Dingwell 1993a; Hess and Dingwell 1996). For calculation of the drop shape relaxation time (Eq. 1), the surface tension was assumed to be 300–400 mN/m. The maximum calculated relaxation time of 120 h was for the lowest-temperature experiments and highest viscosity melts (see Table 2). At high temperatures where losses of alkalis may be significant, samples were held not more than 20 min to provide a stable temperature field in

TABLE 2. Results of surface tension measurements (in mN/m)

T °C (time)	Rhyolite (Armenia)	HPG8	HPG8 + 5 wt% Na_2O	HPG8+ 5 wt% Li_2O	HPG8 + 5 wt% K_2O	HPG8 + 5 wt% Rb_2O	HPG8+ 5 wt% Cs_2O	HPG8 + 20 wt% Na_2O	HPG8 + 10 wt% P_2O_5
1665		305 (20 min)							
1600		304 (20 min)							
1575		300 (20 min)							
1525		298 (25 min)							
1500	374 (20 min)	296 (30 min)							
1464	372 (20 min)								
1450		293 (45 min)							
1398									425 (2 h)
1388	363 (20 min)			281 (20 min)					
1375		289 (75 min)							
1370									426 (3 h)
1360				283 (20 min)					
1350		288 (2 h)	272 (2 min)		240 (20 min)	248 (25 min)	259 (20 min)	272 (20 min)	429 (3 h)
1325					238 (20 min)				
1310	357 (20 min)			287 (20 min)					
1300		284 (6 h)			235 (25 min)		257 (25 min)	273 (20 min)	434 (3 h)
1286	354 (20 min)			290 (20 min)					
1275					234 (25 min)				
1250		283(15 h)			231 (30 min)		255 (1 h)		428 (5 h)
1240	349 (2 h)			292 (20 min)					
1225		282(18 h)			229 (30 min)				439 (10 h)
1200		280(25 h)	270 (5 min)		227 (30 min)	247 (25 min)			441 (24 h)
1185	346 (6 h)								
1175					225 (30 min)				
1145			269 (10 min)	302 (20 min)			252 (5 h)		
1125					221 (45 min)				447 (60 h)
1110				306 (20 min)		246 (1 h)		278 (20 min)	
1093				308 (20 min)					
1080									456 (120 h)
1075					219 (2 h)				
1063				312 (20 min)					
1037				315 (20 min)			250 (24 h)		
1025			268 (2 h)			245 (10 h)	249 (72 h)		
1000					214 (8 h)			279 (20 min)	
989				319 (30 min)					
938				322 (45 min)					
900			267 (17 h)					280 (20 min)	
925					210 (48 h)				
890				327 (50 min)					
800								282 (20 min)	
750								283 (2 h)	
700								284 (8 h)	
650								285 (60 h)	
Const*	245	212	256	412	144	239	221	295	549
Slope*	+0.09	+0.06	+0.01	-0.10	+0.07	+0.01	+0.03	–0.02	–0.09

Note: Before measuring surface tension, sessile drops have been held a specified time (numbers in brackets) at each temperature.
* Data have been fitted to the expression: surface tension (in mN/m) = const (in mN/m) + Slope (in mN/m/°C) * *T*(°C).

the furnace. In a test experiment with HPG8 composition, after keeping a sample at 1650 °C for 2h, the losses of Na_2O and K_2O were still within the analytical error of the microprobe (<0.5 wt%). Losses of alkalis from the surface of a sessile drop have not been estimated directly. The observed variation of sessile drop shapes with time at a fixed temperature is less than the error of a surface tension measurement. We assume that the compositional changes on the surface of sessile drops did not significantly affect the results of our measurements.

The melt density must be known when using a sessile drop method. Densities of haplogranite glasses were determined at room temperature from Archimedean buoyancy determination in toluene and air at 25.5 °C using a laboratory balance (Mettler AE 160) having a precision 10^{-4} g (see Table 1). These densities were extrapolated to higher temperatures using the thermal expansion coefficients determined by Knoche et al. (1995).

Two different procedures were utilized to estimate the surface tension from measured *x*-*z* coordinates of the sessile drop profile. The first one used the *x*-*z* coordinates of the entire meridional section and fitted the measured drop profile to a theoretical one by optimizing the surface tension. The second procedure used measurements of sessile drop parameters at characteristic points (e.g., Ellefson and Taylor 1938) and the tables of Popel et al. (1954), analogous to the tables of Bashforth and Adams (1883).

Estimation of surface tension from the drop size and curvature

There are several methods of fitting the *x*-*z* coordinates of a sessile drop profile to extract the surface tension of the melt. Computer methods to estimate the parameters of a sessile drop from the *x*-*z* coordinates of its profile have some advantage over the method of precise measurement of drop dimensions at a few characteristic points. But this method is difficult to implement when the image of the drop does not exhibit high optical contrast, as often occurs at high temperatures. Several numerical procedures have been developed to calculate surface tension from the shape of sessile or pendant drops (e.g., Maze and Burnet 1969; Rotenberg et al. 1983). The method of fitting that has been used in this study is based on the calculation of the curvature of the sessile drop profile from *x*-*z* coordinates.

The Laplace equation for the equilibrium free surface of a sessile drop can be written as follows:

$$\sigma\left(\frac{1}{R_1}+\frac{1}{R_2}\right)=(\rho_1-\rho_2)gZ+\frac{2\sigma}{R_0} \qquad (2)$$

where σ is the surface tension on the phase boundary between the melt and surrounding gas, R_1 and R_2 are two principal radii of curvature at a point on the free surface, R_o is the radius of curvature at the apex of the drop, ρ_1 and ρ_2 are densities of the melt and the gas phase, and Z is the vertical coordinate of the point on the surface measured from the apex of the drop (e.g., Ellefson and Taylor 1938).

If the vertical (z) and horizontal (x) coordinates of the free surface of a sessile drop are known, the two principal radii of curvature can be expressed via the equation of $Z \propto F(x)$, as follows:

$$R_1(x)=\frac{\left[1+\left(\frac{dZ}{dx}\right)^2\right]^{3/2}}{\frac{d^2Z}{dx^2}} \qquad (3)$$

and

$$R_2(x)=\frac{x\left[1+\left(\frac{dZ}{dx}\right)^2\right]^{1/2}}{\frac{dZ}{dx}}. \qquad (4)$$

The Laplace Equation 2 can be rewritten in a more simple form

$$Z(x) = C_1 \times F(x) + C_2 \qquad (5)$$

where $F(x)$ can be calculated from *x*-*z* coordinates of points on the meridional profile of a sessile drop using Equations 3 and 4. The measured values of $Z(x)$ may be fitted to the linear expression 5, and then from the calculated constant $C_1 = \sigma/(\Delta\rho g)$, the surface tension σ may be estimated for a known melt density.

Determination of the surface tension from sessile drop parameters

In this procedure tables of sessile drop parameters have been used (Popel et al. 1954). These tables contain the meridional diameter L of a sessile drop and the distance Z between meridional diameter and the apex of the drop as a function of the surface tension and density of the drop material. Discussion of the precision of this graphical method can be found in Sangiorgi et al. (1982).

These two methods gave results on the surface tension of the studied haplogranite melts that differ by <5%. In the case of high-temperature measurements (>1200 °C), the computerized method fails. The main difficulty with its implementation is the poor contrast on video images of sessile drops at high temperatures. Therefore, only images obtained at temperatures below 1100 °C were analyzed using the computer methods.

Sessile drop at water pressure

To study the effect of water pressure on the surface tension of melts, measurements of sessile drop parameters on quenched drops have been used. From Equation 1, the relaxation time of a sessile drop shape may be estimated and this puts a restriction on the quench rate. For example, for drops 10 mm in diameter a surface tension of ~100 mN/m and a viscosity of $>5\cdot10^3$ Pa·s, a quench rate of 3 °C/s is enough to preserve a true shape of a haplogranite sessile drop quenched from 1000–1100 °C. Taking into consideration the viscosity of HPG8 melts at water pressures up to 5 kbars (Schulze et al. 1996), the measurements of surface tension by this method for sessile drops of haplogranite melts with 8–9 wt% H_2O quenched in an internally heated gas vessel will be reliable only at temperatures below 1100–1200 °C. Quenching from higher temperatures may affect the shape of quenched drops. This situation is mitigated, however, by the fact that temperature affects the surface tension to a lesser extent than the water solubility in the surface layer of a drop.

For experiments under pressure, sessile drops of HPG8 com-

position were prepared as follows. Ground powder of HPG8 glass was placed in open Pt capsules (5 mm in diameter and 10 mm long) and fused at temperatures of 800, 900, 1000, 1100, and 1200 °C at 3 kbar of water pressure, and then at 1000 °C and 1, 2, 3, and 4 kbar water pressure for ~120–150 h. Water pressure was generated in a vertical gas vessel with a Bridgman-type cold seal and an internal heater (three section Pt furnace) at the Vernadsky Institute of Geochemistry, Moscow. Temperature control was provided by 3 S-type Pt-PtRh thermocouples believed to be accurate to ± 5°C. The volume where capsules were placed was filled with distilled water and closed with a thin rubber membrane. The volume with water is separated from the compressed gas by a layer of mercury kept in a cup that is located in a cold zone of the vessel. Water pressure is created by nitrogen gas acting through a free surface of mercury and the rubber membrane to produce high water pressure in the reactor chamber. Water content in all prepared samples was presumed equivalent to weight losses (precision ±0.1 mg) after melting small chips (ca. 0.5 g) at 1350 °C and 1 bar overnight in a box furnace. For the surface tension measurements, cylinders of hydrous haplogranite glass were mounted vertically on a graphite substrate in the reactor chamber in such a way that they have a free surface in contact with water. After remelting, the cylinders developed a sessile drop shape. Experiments were conducted at 1000 °C and 1, 2, 3, and 4 kbar of water pressure, and at a fixed pressure of 3 kbar and 800, 900, 1000, 1100, 1200 °C for ~0.5 – 1 h each. Quenched sessile drops were photographed and parameters of their shape were estimated from their photo images by using the tables described above (Popel et al. 1954).

Results and discussion

Temperature dependence of surface tension at 1 bar and effect of alkalis

Results of the surface tension measurements in haplogranite melts with the excess of 5 wt% of alkali oxides is shown in Figure 1B. The temperature interval of measurements is different for HPG and HPG melts with alkalis due to the effect of alkalis on the glass transition temperature of melts (Hess et al. 1995). Most compositions exhibit a weak positive temperature dependence of the surface tension (see Table 2): +0.06 mN/m°C for HPG, +0.01 for HPG + 5 wt% of Na_2O, +0.07 for HPG + 5 wt% K_2O, +0.03 for 5 wt% Cs_2O, and +0.001 for 5 wt% Rb_2O; but –0.1 for HPG + 5 wt% Li_2O, and –0.02 for HPG + 20 wt% Na_2O. The surface tension of HPG melt increases significantly with the addition of P_2O_5 and the temperature dependence is negative –0.09 mN/m/°C (Fig. 1C). Armenian rhyolite exhibits the same temperature dependence of the surface tension as HPG melt (+0.09 mN/m°C, Fig. 1C). The mean value of the surface tension increases with excess alkalis or decreased silica content in the melt.

A positive temperature dependence of the surface tension implies that the surface entropy is negative. This might be explained by the dissolution of gas species in the surface layer or by the diffrentiation of the free drop surface into sublayers with differing chemical compositions. The temperature dependence of the surface tension of silicate melts is, in general, small and positive (+0.05 to +0.07 mN/m/°C, see King 1951; Popel and Esin 1956), similar to that which we have observed here for HPG melts. Our experiments show that addition of 5 wt% of Li_2O or 10 wt% of P_2O_5 results in a negative temperature dependence of the surface tension. At small concentrations of the alkalis, the thermal coefficient of the surface tension is positive, whereas at high concentrations it becomes negative. Comparing melts with the same mole fraction of alkalis (10 mol%), the highest surface tension is observed in Li_2O-SiO_2 melts (300 mN/m at 1300 °C), and the lowest is in K_2O-SiO_2 melts (240 mN/m, at 1300 °C, see Shartsis and Spinner 1951). Our data confirm these general effects of alkalis on the surface tension of silicate melts.

Effect of water

Results of the surface tension measurements in hydrous haplogranite melts are shown in Figure 2. At a fixed temperature (1000 °C) different water pressures result in different solubilities of water (Table 3). The pressure effect on the surface tension is quite significant. The largest decrease of surface tension, from 268 mN/m at 1 bar to 65 mN/m at 4 kbar, occurs at very small water pressures, which corresponds to ~0.2 wt% water dissolved in the melt. The overall decrease of the surface tension (at 1000 °C) fits the equation (Fig. 2a):

$$\sigma[\text{mN/m}] = 236.6 \cdot \exp\{-0.35 \cdot P[\text{kbar}]\} \quad (6)$$

The surface tension of a dry haplogranite melt is 4.5 times larger than that under 4 kbar of water pressure. The effect of temperature at fixed pressure is shown in Figure 2b. The water content varies slightly with the temperature from 8.8 to 9.2 wt% at 1200 and 800 °C, respectively. At this practically constant water content, the temperature dependence fits an Arrhenius relationship with an activation energy of 11 kJ/mol. The activation energy of the surface tension calculated for water-free haplogranitic melt from the 1 bar study is ~4.5 kJ/mol.

Table 3. Surface tension measurements of haplogranite melt under water pressure

	P (Kbar)*					*T* (°C)†					
	0.001	1	2	3	4	800	900	1000	1100	1200	
C_{H_2O}‡	<0.03§	7.20	7.52	8.91	10.42	9.26	8.90	8.90	8.91	8.92	8.79
σ (mN/m)	268§	135	98	90	65	73	84	90	97	103	

Note: Surface tension was estimated within ±0.5 mN/m. Chemical composition of haplogranite melt (HPG8) is given in Table 1.
*Effect of water pressure at T = 1000 °C.
†Effect of temperature at P_{H_2O} = 3 Kbar.
‡Estimated from weight losses within ±0.1 wt% after annealing of samples at 1 bar 1400 °C.
§ Data extrapolated from 1 bar measurements.

From the data on water content in HPG sessile drops and the surface tension, the effect of water solubility is estimated as –20 ± 10 mN/m/wt%H_2O (Fig. 2c). The effect of water on the surface tension is certainly a non-linear function of solubility. For example, the decrease of surface tension of soda-lime-silica melt at 450–700 °C due to the presence of water vapor in the atmosphere is from 290–310 mN/m in vacuum to 200–210 mN/m at 12 mm Hg of partial pressure of H_20 (Parikh 1958). Water molecules affect the surface tension of silicate melt more than any other gas (SO_2, air, N_2) because of their high dipole moment ($2 \cdot 10^{-18}$ e.s.u., Parikh 1958).

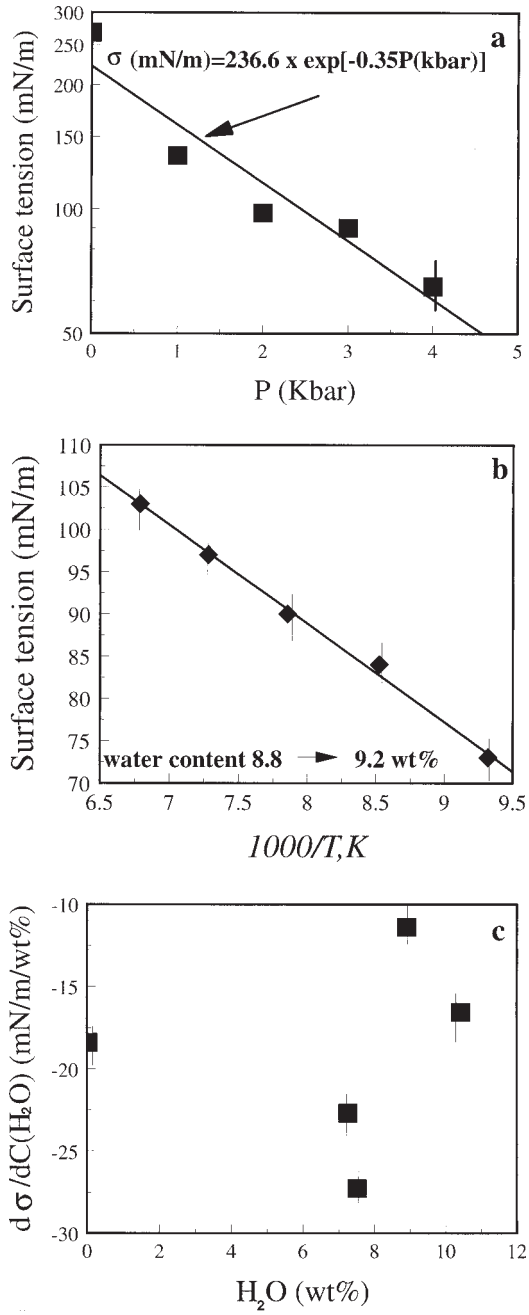

FIGURE 2. (**a**) Effect of water pressure on surface tension of HPG melt at 1000 °C. Solid line is Equation 6. (**b**) Effect of temperature on surface tension of HPG melt at P_{H_2O} = 3 kbar of pressure. (**c**) Effect of water content (C_{H_2O}) on the change in surface tension of HPG melt at 1000 °C.

Correlation between surface tension and expansivity of melts

If there is no layering of the surface with temperature, then the volume expansivity and the surface expansivity (thermal coefficient of the surface tension) have to be correlated (Shartsis and Spinner 1951). Figure 3 demonstrates the correlation between the temperature coefficient of the surface tension from this study and the thermal expansivities of haplogranite melts (Knoche et al. 1995). The general tendency noted for silicate melts in previous studies is that higher thermal expansivity correlates with higher negative thermal coefficient of the surface tension (e.g., Fig. 3). The thermal expansion coefficient of the Armenian rhyolite has been measured in the push-rod dilatometer as $2.5 \cdot 10^{-6}$ /°C. The correlation between thermal expansivity and the temperature dependence of the surface tension may be approximated by the equation

$$\alpha[\mathrm{grad}^{-1}] = 5.9 \cdot 10^{-5} - 2.8 \cdot 10^{-4} \cdot \frac{d\sigma[\mathrm{mN/m}]}{dT[^\circ\mathrm{C}]}. \qquad (7)$$

The composition HPG + 10 wt% P_2O_5 (not plotted) does not correlate with the thermal expansivities of haplogranitic melts with excess alkalis. This may be due to the anomalous surface tension of P_2O_5 melt which itself possesses very low surface tension with a strong negative temperature dependence (Kingery 1959). HPG and natural rhyolite compositions have practically the same surface tension as fused silica, 280–290 mN/m at 1100–1300 °C (Parikh 1958). In general, the temperature coefficient of the surface tension correlates with the average field strength of added cations (Z/R) for compositions having about the same silica content (King 1951; Walker and Mullins 1981).

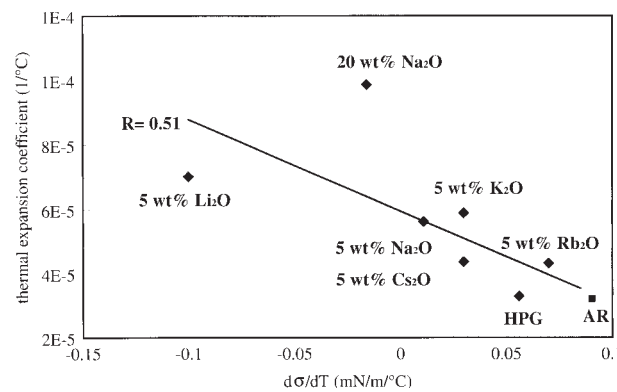

FIGURE 3. Correlation between thermal expansion of haplogranitic melts (closed diamonds) + Armenian rhyolite (closed square) and temperature dependence of surface tension. Thermal expansion coefficient is taken from Knoche et al. (1995). Solid line is Equation 7.

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