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**EXPERIMENT PLAN FOR CHARACTERIZATION OF THE
PROPERTIES OF MOLTEN ROCK AT ATMOSPHERIC AND
ELEVATED PRESSURES: MAGMA ENERGY RESEARCH
PROJECT**

P. J. Modreski

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ABSTRACT

Knowledge of the properties of molten rock (magma) is of importance to the Magma Energy Research Project of Sandia Laboratories. Facilities have been set up at Sandia to study the physical properties, chemistry, and corrosive nature of magma to 1600°C and from atmospheric pressure to 4 kbar (400 MPa). Experiments at atmospheric pressure are being done in the presence of multi-component gas mixtures to control the chemical activities of oxygen and sulfur. The high pressure apparatus includes "cold-seal" small volume pressure vessels (to 1100°C and 1 kbar) and a large (750 cm³ sample volume) internally heated pressure vessel (to 1600°C and 4 kbar). The large vessel contains a number of penetrations for electrical leads and pressure lines and is linked to a computer for data acquisition and control of experiments.

Water and other dissolved volatiles (CO₂, CO, SO₂, S₂, H₂S, HCl, HF) have significant effects on all the properties of magma, and these effects will be studied in the high pressure apparatus. Phase equilibria, viscosity, electrical conductivity, and materials compatibility will be the first properties to be examined under pressure. This report includes a review of the nature and chemical basis for the effects of dissolved volatiles on these properties of magma.

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INTRODUCTION AND ASSESSMENT OF NEEDED MEASUREMENTS

This report describes the laboratory experiments on igneous rock melts that are planned or in progress at Sandia, the rationale for such experiments, and the apparatus with which they will be performed.

The Magma Energy Research Program of Sandia Laboratories is an investigation of the feasibility of extracting thermal energy from underground bodies of molten rock (magma). The 1975 Magma Workshop, an invitational meeting sponsored by Sandia Laboratories in March, 1975, included a working group which evaluated the "state of knowledge, relevance, and priority for research of various chemical and physical parameters" of molten and hot solid rock [1]. Various physical and chemical properties were evaluated for their relevance to:

1. Exploration for magma bodies. This emphasizes those properties that relate to remote geophysical detection of magma bodies, such as electrical conductivity and the seismic properties of magma and of the hot solid rock which surrounds it.
2. Development (i.e., drilling toward and into a magma body). The mechanical properties of rock near its melting point and the nature of the corrosive environment near a magma body are the properties most relevant to development.
3. Heat extraction. The important properties are those relating to heat transfer by conduction and convection (i.e., thermal conductivity, viscosity, and density). For an alternate "open system" heat extraction concept involving direct injection of a fluid (water) into magma, phenomena such as gas solution and exsolution rates, surface tension, leaching and hydrothermal alteration, and change in the properties of the magma due to solution of water would be important.

The highest priorities for research (based on the combination of inadequate knowledge of a property plus high relevance to exploration-development-heat extraction) were assigned to:

composition and properties of the volatile ("fugitive") constituents
in magma (the elements H, C, O, S, Cl, and F)
phase relations and properties of melts in the presence of aqueous
fluids containing components such as NaCl and NaF
heat transfer coefficient, heat capacity, and thermal diffusivity
of magma

viscosity, density, and thermal expansivity of the melt phase and of bulk magma (liquid plus suspended crystals or gas bubbles) seismic, electrical, and magnetic properties of magma strength, "ductility," and "permeability" of magma materials behavior in the chemical environment of magma

In accordance of the recommendation of the Workshop and with the advice of Sandia's Magma Advisory Panel, we have decided to concentrate on experiments to measure the effects of pressurized volatile atmospheres on the physical properties of molten rocks, materials compatibility studies, and selected aspects of the chemical equilibria between silicate melt and a gas phase. Most of the properties of molten rock that are of interest have been at least approximately determined at atmospheric pressure in the laboratory or in the field [2], but relatively little work has been done to date at the elevated pressures which are required to maintain dissolved volatiles in the melts.

The experimentation at Sandia will be done both at high pressures (to 4 kbar) and at atmospheric pressure. The atmospheric pressure work will be done mainly to prove out the experimental techniques to be used at the elevated pressures and to provide baseline data for comparison with the results of the high pressure studies. It is worth noting that there remain a number of areas in which careful measurements at atmospheric pressure alone would be of real value; for example, studies of the viscosity and other physical properties of multiphase magma systems (melt plus suspended crystals or gas bubbles).

The initial experiments will consist of work on phase equilibria and gas solubility studies, viscosity, electrical conductivity, and materials compatibility. The experiments will be done on a series of igneous rock compositions which include basalt (1971 Kilauea tholeiite, 50 wt. % SiO_2), andesite (Mount Hood, Oregon, andesite, 61 wt. % SiO_2), and rhyolite (Newberry Caldera, Oregon, rhyolite obsidian, 73 wt. % SiO_2). The outline of experiments as described here was prepared after consultation with a number of scientists who are working in the area of experimental petrology [3].

REVIEW OF THE EFFECT OF VOLATILES ON THE PROPERTIES OF MAGMA

The Nature of Magmatic Volatiles

The principal volatile components to be studied in the experiments are water, carbon dioxide, and sulfur ($\text{H}_2\text{S}/\text{S}_2/\text{SO}_2$). Some work will also be done with chlorine (as HCl) and fluorine (HF). Water is quite soluble in silicate melts (about 3 to 4 wt. % at 1 kbar pressure [4], Fig. 1), and it is the most abundant volatile in natural magmas, ranging in concentration from about 0.25 to 0.5 wt. % in tholeiitic basalts to as much as 5% or more in rhyolitic magmas at depth [5]. Of the volatiles present in magmas, water has the greatest effect on the properties of the melts. Dissolved water significantly lowers the solidus and liquidus temperatures of silicate melts (Fig. 2). Water dissolves by breaking Si-O-Si linkages, thereby depolymerizing the melts and decreasing their viscosity [6]:

where M is a non-framework (not tetrahedrally coordinated) cation such as Na, Ca or Fe. The solubility of water in silicate melts is found to be proportional to the square root of the fugacity of water up to a mole fraction of water of approximately 0.5 (using the definition of Burnham [7] in which 1 mole of aluminosilicate melt is that which contains one gram-atom of exchangeable cations). Several breaks in slope of the solubility curve of water in sodium aluminosilicate melts have recently been noted above 1.5 kbar (which corresponds to a mole fraction of H_2O of 0.5) in $\text{NaAlSi}_3\text{O}_8$ melt; these may correspond to changes in the structural mechanism for solution of water in the melts, which has been interpreted to involve an association of dissolved water with Na and Si but not Al [8].

The solution of carbon dioxide in silicate melts has a structural effect opposite to that of water. Both $\text{CO}_3^{=}$ ions and molecular CO_2 exist in the melts, with a higher proportion of $\text{CO}_3^{=}$ in the more basic melts [9]. The formation of $\text{CO}_3^{=}$ produces new bridging oxygen atoms, increasing the degree of polymerization of the melts:

Figure 1. Data is from various sources, listed in Ref. 27.

Figure 2.

The solubility of carbon dioxide in silicate melts is less than that of water by a factor of (by weight) five or ten at a given pressure [10]. The actual carbon dioxide content of mid-oceanic basaltic magmas has been found to be on the order of 800 to 1600 ppm [11].

Sulfur exists as a variety of species in magma and magmatic gas. SO_2 , H_2S , and S_2 are the most important species in the gas phase in equilibrium with magma [12], while within the melt sulfur is believed to exist dominantly in the sulfide form covalently associated with ferrous iron [13]. Sulfate sulfur is an important species in melts under conditions more oxidizing than those normally encountered in magmas [14]. The common separation of small amounts of iron-copper-nickel sulfide globules from natural basalts [15] is indicative of the existence of $\text{S}^{=}$ in the melt. Because of the Fe-S association, the solubility of sulfur in silicate melts has a positive dependence on the iron content [16]. Sulfur also shows increasing total solubilities at both high and low oxygen fugacities (under which $\text{SO}_4^{=}$ and $\text{S}^{=}$ respectively are stabilized), with a solubility minimum at an intermediate oxygen fugacity (about 10^{-7} bar at 1250°C) [17]; this minimum lies close to or slightly above the oxygen fugacity expected in natural magmas (i.e., about 1.3×10^{-8} bar for a magma on the fayalite-magnetite-quartz buffer at 1250°C). The solubility (total sulfur) of sulfur in melts having iron contents and oxygen fugacities approximating those of natural basaltic magma at its liquidus temperature has been measured to be in the range 100 to 1000 ppm at atmospheric pressure [18]. Actual concentrations of sulfur have been found to be on the order of 800 to 1000 ppm in submarine basaltic lavas and between 100 to 3000 ppm in some continental basalts and andesites [19].

HCl is the stable form of chlorine in magmatic gases [20], and chlorine within magmatic melts presumably exists as Cl^- and possibly molecular HCl. The partitioning of HCl between a gas and a silicate melt at low pressures very strongly favors the melt as compared to other volatiles; the solubility in basalt at 1200°C is reported to be 1.5 wt. % HCl at $P_{\text{HCl}} = 1 \text{ atm}$ [21]. However, in the presence of a supercritical aqueous fluid phase under pressure, chlorine (as Cl^-) is partitioned quite strongly into the aqueous phase in preference to the silicate melt; partition coefficients ($m_{\text{Cl}^-, \text{melt}}/m_{\text{Cl}^-, \text{aq.}}$) have been found to be on the order of 0.1 to 0.01 for granitic melts at 700 to 750°C and 2 to 8 kbar [22]. The chlorine content of natural magmas appears

to vary between about 50 to 2000 ppm [23]. The HCl component of magmas will be of particular interest because of its effect on corrosion processes.

Fluorine, which as F^- can substitute for oxygen anions in both silicate melts and in crystalline silicate minerals, also has a very high solubility in silicate melts and is retained by a cooling magma in preference to a co-existing aqueous phase more so than is chlorine [24]. The fluorine content of some Hawaiian basalts has been found to be in the range 240 to 800 ppm [25].

Phase Equilibria and Gas Solubilities

A large number of experimental studies have been performed over the years on the phase relations of numerous igneous rock compositions at pressures ranging from atmospheric to about 50 kbar [26]. The application of pressure alone raises the melting temperature of silicate compositions by approximately 10°C per kilobar, but this effect is small compared to the depression of melting temperatures by volatiles which dissolve in the melts. The existing studies have been done under volatile-absent conditions and also in the presence of H_2O , CO_2 , and $\text{H}_2\text{O}-\text{CO}_2$ mixtures, in about that order of thoroughness.

Numerous measurements have been made on the solubility of water in rock melts of various compositions from pressures of 1000 bars up to 10 kbar or more [27] and also on pertinent synthetic and simplified compositions [28]. The reliable data are still quite limited and for most compositions only a few data points exist; however, when solubilities are computed on a molar basis according to the method of Burnham, the compositional variation in H_2O solubility is very small [29]. The temperature coefficient of H_2O solubility is also very small, apparently negative at pressures less than 10 kbar [30] though the temperature effect is often smaller than the estimated error in the solubility determinations.

Carbon dioxide solubility has been studied a great deal in recent years [31]; most measurements have been made in the 10 to 30 kbar pressure range. In contrast to water, the compositional dependence of CO_2 solubility has been found to be significant, with higher solubilities in more basic (i.e., less siliceous) melts, and the temperature coefficient of solubility is positive. Some solubility measurements have also been made for gas mixtures on the $\text{H}_2\text{O}-\text{CO}_2$ join [32]; CO_2 has a higher solubility in melts containing a small amount of water than in anhydrous melts, probably because of the opposite

structural effects of H_2O and CO_2 in the melts; the additional non-bridging oxygen atoms formed by the solution of the water (Eq. 1,2) provide additional sites with which molecular CO_2 can react to form CO_3^- (Eq. 3). Sulfur and HCl have been studied almost exclusively at atmospheric pressure with the exception of some measurements recently reported on the solubility of SO_2 in $\text{NaAlSi}_3\text{O}_8$ melt at 10 to 30 kbar and 1450 to 1525°C [33]. A small amount of work has been done on the effect of mixed volatiles on phase equilibria (i.e., $\text{H}_2\text{O}+\text{HCl}$, $\text{H}_2\text{O}+\text{HF}$, $\text{H}_2\text{O}+\text{NH}_3$, and $\text{H}_2\text{O}+\text{SO}_3$) [34], but aside from the $\text{H}_2\text{O}-\text{CO}_2$ studies this has not included solubility determinations.

Viscosity

The viscosity of magma is an important parameter in calculations relating to convective heat transfer. It is also important in understanding or modeling such phenomena as the upward intrusion of magma, crystal settling, and the flow of lava on the surface. Viscosity can be related to the molecular structure of silicate melts [35] and to other mechanical and transport properties.

Numerous studies have been made of the viscosity of silicate melts of various compositions, and partial molar coefficients have been derived for the computation of Newtonian viscosity as a function of temperature and melt composition [36]. However, relatively few measurements have been made on the viscosity of volatile-containing melts under pressure [37], and this should be a useful area for experimentation. The viscosity of magmas ranges from about 10^2 to 10^3 Poise ($= 10^2$ to 10^3 dyne sec $\text{cm}^{-2} = 10^1$ to 10^2 Pa sec) for basaltic magma at its liquidus temperature to about 10^{10} Poise for glassy rhyolite at its solidus temperature. From the work which has been done, it is clear that it is the absolute amount of a dissolved volatile (e.g., water) rather than the total pressure that determines viscosity. Some measurements have been made on anhydrous molten rocks up to 30 kbar [38]; although conflicting data have been reported, it appears most likely that viscosity decreases slightly with increase in total pressure and that the effect of absolute pressure will be almost negligible in the 0-4 kbar range accessible in experiments at Sandia. The viscosity of granitic or rhyolitic melts decreases drastically with added water (e.g., from about 10^9 to less than 10^6 Poise estimated at 1150°C for an addition of 2 wt. % H_2O), but the effect is much less in the more basic compositions; the viscosity of olivine basalt is reported to be lowered only slightly under the same conditions [39](Fig. 3).

Figure 3.

There are essentially no data on the effect on viscosity of volatiles other than water.

Electrical Conductivity

Conductivity is of fundamental importance to the interpretation of remote geophysical sensing data which can be used to recognize subsurface bodies of magma, as in the work that has been done at Kilauea Iki crater [40]. Silicate melts are ionic conductors, and conductivity data can be related to ion mobilities and to the structure of the chemical species present in the melts [41]. A relatively small number of measurements have been made on the conductivity of molten rocks at atmospheric and elevated pressures [42] and the existing data on conductivity under pressure in the presence of volatiles are minimal [43]. The conductivities of igneous rocks at melting temperatures are on the order of 10^{-2} to $10^1 \text{ ohm}^{-1} \text{ m}^{-1}$, increasing rapidly with increasing temperature through the melting interval.

APPARATUS

The following types of apparatus have been set up at Sandia for experimentation on lavas at atmospheric and elevated pressures:

Atmospheric Pressure Gas-Mixing System

A horizontally mounted tube furnace through which gases circulate within a mullite tube is being used primarily for materials compatibility experiments (Fig. 4). Mixtures composed of CO_2 , CO , H_2O , and SO_2 are being used; other gases, such as H_2 , H_2S , and HCl could be added as desired. The maximum temperature is 1200°C ; the length of the isothermal zone ($\pm 5^\circ\text{C}$) within the 5.08 cm i.d. tube is about 13 cm. The gases are metered through calibrated flow meters with the exception of water, the flow of which is calculated from the vapor pressure of water in a constant temperature bath through which one of the other gases or argon is bubbled as a carrier. Lava samples for the compatibility tests are usually contained in high purity (99.8% Al_2O_3) alumina crucibles, which are relatively non-reactive to the lava for runs of 10 to 100 hours duration. Due to solution of Al_2O_3 in the lava, such crucibles are not suitable for careful phase equilibrium studies on the lavas. This system presently has no provision for rapid quenching, and the samples are cooled fairly slowly (about 4°C min^{-1}) by shutting off the furnace power. The system is not equipped with an oxygen fugacity probe, and the concentrations and activities of gas species at temperature are calculated from the input mixture assuming equilibrium conditions.

Atmospheric Pressure Rapid Quench System

A 1250°C furnace has been set up for experiments on lava or other samples in a controlled gas atmosphere (Fig. 5). CO_2/CO , CO_2/H_2 or similar gas mixtures flow through a mullite tube within a vertically mounted tube furnace; lava samples are suspended in the gas stream by hanging a drop of melt from a loop of fine platinum wire (about 0.125 mm diam.) attached to a quartz rod. This technique facilitates rapid equilibration between the lava and the gas atmosphere, and minimum contamination of the sample by reaction with the container material [44]; some loss of iron from the sample does occur by reduction of iron and diffusion of Fe^0 into the platinum wire. The samples are quenched rapidly in air by pushing the quartz rod carrying the samples out through the bottom of the furnace. An air reference ZrO_2 solid electrolyte oxygen fugacity electrochemical cell [45] is incorporated within the furnace

CONTROLLED ATMOSPHERE TEST SYSTEM

Figure 4.

RAPID QUENCH SYSTEM

Figure 5.

for direct measurement of oxygen fugacity adjacent to the sample, as a check on that calculated for a given gas mixture at equilibrium. It is intended that this system generally be kept "clean," using only $\text{CO}/\text{CO}_2/\text{H}_2/\text{H}_2\text{O}$ gas mixtures without any sulfur-containing gases.

The main use of this apparatus will be for phase equilibrium studies of the lavas (melting range, crystalline phases present at equilibrium, etc.); a controlled gas atmosphere is essential to regulate oxygen fugacity in these experiments. These data will provide baseline information for comparison with phase relations in the presence of volatiles at higher pressures, and for planning and interpretation of the physical properties measurements which are sensitive to the degree of crystallization of the lava. This apparatus will also be useful for atmospheric pressure duplication of some of the physical properties measurements to be made at high pressures, such as electrical conductivity and viscosity.

Cold-Seal (1 kbar) Pressure Vessels

Two TZM alloy (Mo - 0.5%Ti - 0.08%Zr) cold-seal pressure vessels are presently set up for phase equilibrium experiments on lavas plus volatiles under pressure and for initial compatibility tests in pressurized gas atmospheres. The vessels are externally heated in a resistance furnace, pressurized with argon, and are of relatively small internal volume (6.4 mm diam. x 286 mm total length). Maximum operating temperature is 1100°C and the maximum operating pressure in the present setup is 1000 bars although the system could be replumbed to achieve the upper operating limit of the pressure vessels, 3000 bars at 1100°C . An inconel sheath purged with N_2 -2% H_2 protects each vessel from oxidation. The system is currently pressurized by condensing argon into a pressure reservoir at liquid nitrogen temperature and warming the reservoir to produce the desired gas pressure, but a diaphragm-type argon compressor is being added to the system. Temperature is measured with a thermocouple either inserted internally or attached to a well in the outside of the sheath; the external readings are related to the internal temperature by calibration runs. The length of the hot zone ($\pm 10^\circ\text{C}$) within the vertically oriented vessels is about 3.5 cm.

One of the vessels is presently equipped with a "Shaw membrane" [46] to control oxygen fugacity within water-containing capsules via diffusion of hydrogen through a platinum tube connected to an external reservoir of

hydrogen at known pressure (P_{H_2} typically about 3 to 15 bars)(Fig. 6).

Experiments are normally run with solid and gaseous reactants enclosed within thin-walled capsules of gold (below 1050°C) or $Ag_{50}Pd_{50}$ tubing. Volatiles can be added to the experiment capsules in the form of solid or liquid phases which vaporize or decompose upon heating (e.g., water, oxalic acid, silver oxalate, sulfur, silver sulfate) to give the desired atmosphere. The small volume available puts a constraint on the amount of volatile material that can be sealed within a capsule to maintain a gas phase of constant composition during the experiment, particularly with regard to depletion of sulfur by reaction with metals in materials compatibility experiments. This problem can be overcome to some extent by using oxide phase assemblages to buffer oxygen fugacity (e.g. Fe_2SiO_4 - Fe_3O_4 - SiO_4 , Ni-NiO, FeO- Fe_3O_4 , etc. [47]) and sulfide phases such as pyrrhotite, $Fe_{1-x}S$, to buffer sulfur fugacity.

4 kbar Pressure System ("Magma Simulation Facility")

This facility (Fig. 7) consists of a 4 kbar large volume (18 cm i.d. x 40 cm length) internally heated pressure vessel built by Autoclave Engineers. The vessel is pressurized with argon using a Harwood DA-4 two-stage compressor. An internal furnace is now being built for the vessel by Autoclave Engineers; this will be a 1600°C molybdenum single-zone resistance furnace employing a convective heat transfer design to heat a 10 cm diam. x 10 cm long hot zone ($\pm 10^\circ C$) located above the heating elements. The system is located in a blast cell (Bldg. 9938) and will be operated remotely from an adjacent control room (Bldg. 9939) because of the blast hazard of the large volume of pressurized argon. An on-line computer will be used to collect and process data and to control the operating parameters and safety interlocks of the system. The computer is a Hewlett-Packard 2171A with 64 kbyte memory, a 15 Mbyte disc, and RTE-III operating system software; it is interfaced with an HP 9648A CRT/graphics terminal, a Tektronix 4632 video copy unit, an HP 9866A thermal printer (240 lpm), and an HP 9603R remote measurement and control station with digital and analog input/output channels.

The relatively unique features of this system are the large volume permitting both large samples and the use of a large number of electrical measurement circuits or mechanical devices for simultaneous measurements within the pressure vessel [48]; the availability of the computer for data handling; and the planned future incorporation of a system for introducing

SHAW MEMBRANE H_2 FUGACITY CONTROL

Figure 6.

MAGMA SIMULATION FACILITY

Figure 7. Schematic layout of Magma Simulation Facility

(and sampling or replenishing) multicomponent gas mixtures to an interior chamber within the pressure vessel. The furnace now under construction (to be completed Feb. 1979) will include ports for pressure lines which can be used in the future for the introduction or removal of gases. Full operation with multicomponent gas mixtures will require (Fig. 8):

1. A suitable inert chamber within the furnace to contain the "reactive" gas mixtures and to isolate them from the argon which fills the rest of the vessel. A molybdenum chamber with a liner of platinum or a similar noble metal alloy might be suitable.
2. A gas delivery system to mix, compress, and supply complex gas mixtures to the pressure vessel. L. Baudoin [49] has designed a magnetically driven high pressure pump suitable for circulating gases at high pressure through such a chamber.
3. A pressure balancing cell to maintain the pressure differential between the internal chamber and the rest of the pressure vessel at a tolerable value (e.g., to within a few to a few tens of PSI).

Once the internal chamber is operating it can be used for:

1. Continuous supply of controlled gas atmospheres to buffer the activities of volatile species over simulated magma samples.
2. Compatibility experiments of long duration.
3. Experiments on the interactions between introduced gases and liquid rock (e.g., phenomena of bubble formation, fluid injection, magma fuels generation, etc.).

Prior to operation of the sealed chamber, experiments on volatile-containing melts will be made using samples within sealed noble metal tubes, as is the conventional technique for hydrothermal experimentation. It should be possible to insert a Shaw membrane within the vessel to control hydrogen fugacity, and also operate a ZrO_2 electrochemical oxygen potential cell with a solid buffer internal reference [50] to measure oxygen fugacity within the vessel or within the internal chamber. The temperature capability of the system ($1600^\circ C$) will permit measurements to be made on magma both within the crystallization interval and for several hundred degrees above the liquidus temperature. This will allow, for example, activation energies to be calculated from the temperature dependence of a property over a significant temperature interval within the completely liquid region.

HIGH PRESSURE MELT + GAS CHAMBER

Figure 8. Schematic Drawing of containment vessel for reactive gas atmospheres within 4 kbar pressure vessel.

EXPERIMENTS

Phase Equilibria and Gas Solubilities

It is necessary to determine the equilibrium phase relations within the melting ranges of the three lavas to provide baseline information for the interpretation of and the selection of conditions for all the succeeding experiments. The phase relations will first be determined at atmospheric pressure under conditions of controlled oxygen fugacity in the rapid quench furnace. The solidus to liquidus temperature range is from approximately 950° to 1050°C for the rhyolite and from approximately 1000° to 1200°C for the basalt; that of the andesite is intermediate. These equilibrium studies will be extended to include determinations of the phase relations of these lavas with volatiles--initially and most importantly H₂O--added under pressure in both the cold-seal and the 4 kbar apparatus (Fig. 9,10). Saturation in water at $P_{H_2O} = 4$ kbar will lower the solidus temperatures of the lavas by 200 to 300°C.

The exact solidus temperature and the phase relations very close to the solidus tend to be difficult to determine accurately because of the difficulty of detecting small amounts of liquid (quenched to a glass) in the experimental runs and because of the slowness of the reactions which produce small amounts of rather viscous liquid near the solidus. To be certain of true approach to equilibrium, experiments should be made to verify that starting charges of both crystalline and glassy reactants yield the same result. To properly reproduce actual magmatic conditions, these experiments should be carried out under a gas atmosphere of appropriate oxygen fugacity; this will be done using the flowing gas mixtures at atmospheric pressure and (at first) either sealed tubes containing "buffer" assemblages or a Shaw membrane at the elevated pressures. Equilibrium relations are particularly difficult to determine in rhyolitic compositions because the high viscosity of the melt results in slow rates of crystallization or of homogenization. Determination of phase relations near the liquidus can also present problems because of the metastable formation of crystalline phases during the quenching process; melts do not necessarily quench to glasses, especially the water-containing basaltic melts of relatively low viscosity.

Measurements of the solubilities of volatile components in molten igneous rocks are important of themselves because they provide fundamental data

(a)

(b)

Figure 9. Basalt (1971) Kilauea tholeiite) heated in $\text{Ag}_{50}\text{Pd}_{50}$ capsules at 1100°C , $P=500$ bars for 24 hours in cold-seal pressure vessels. Sample in (a) is water-free and in (b) contains 5 wt.% added water. The hollow at the top of the capsule in (b) is a vapor bubble, the presence or absence of which can be used in determining the solubility of gases in the melt. (6X)

(a)

(b)

Figure 10. Photomicrographs of the basalt samples shown in Fig. 9, illustrating the increased degree of melting in the presence of water. (a) water-free charge composed of stable crystals of pyroxene (light) and plagioclase (dark) in a groundmass which was molten during the run. (b) dendritic pyroxene crystals formed during quenching of the basalt which was nearly completely molten during the run; the euhedral light-appearing crystals are iron-titanium oxide. Polished section, reflected light. (500 X)

relating to the calculation of gas phase compositions in equilibrium with melts, the effect of dissolved volatiles on phase equilibria, and on the nature and thermodynamic activity of solute species present in volatile-containing melts. Solubility measurements are also important in determining boundary conditions to the studies to be made of the physical properties of volatile-containing melts. The solubility measurements will have to be done in the pressure apparatus, although some work on dissolved sulfur, HCl, and HF can be done at atmospheric pressure.

There is a need for good data on the solubility of all the important magmatic volatiles (H_2O , CO_2 , $\text{SO}_2/\text{H}_2\text{S}/\text{S}$, HCl, HF) at pressures of a few kilobars, and particularly for data relating to the partitioning of volatiles between melt and gas phases in systems containing more than one volatile component. The experimentation on H_2O and CO_2 solubility that is in progress elsewhere (as at the Geophysical Laboratory of the Carnegie Institution) is largely at pressures of 10 to 40 kbar and temperatures on the order of 1300° to 1700°C, and is directed toward knowledge of the conditions under which magmas are formed at great depth within the earth's upper mantle. The work to be done at Sandia at modest pressures of up to 4 kbar will be related more to the behavior of relatively low concentrations of volatiles within magmas in the earth's crust, and to the separation of volatiles from cooling and crystallizing magmas.

The techniques that have been used to measure solubility of gases in molten rocks involve equilibrating a molten sample with a known gas atmosphere and either analyzing the quenched melt for the content of the dissolved volatile or examining a series of quenched samples with varying total volatile contents for the presence or absence of gas bubbles, indicating saturation. Recently beta-particle tracks from radioactive carbon (^{14}C) and sulfur (^{35}S) doped into melts have been used effectively to measure the concentrations of C- and S-containing volatiles in melts [51]. Since equilibration of large volumes of melt with a gas phase is controlled by diffusion through the melt and may be rather slow, the use of large samples will normally not be advantageous in these experiments. The 1 kbar cold-seal pressure vessels will be useful for some of the volatile solubility work but much of it will require the 4 kbar vessel, where the ability to run a number of sealed tubes simultaneously will be useful.

In addition to solubility measurements on the most abundant magmatic volatiles, data on the solubilities of some of the inert or inert-behaving gases (e.g., Ar, N₂, He) would also be very useful for the interpretation of the degassing of natural magmas within the earth's crust; only a very few such measurements exist [52]. Work on the solubility measurements will of necessity proceed together with compatibility experimentation to determine suitable encapsulating materials for the potentially corrosive mixed volatile compositions containing S and Cl.

Viscosity Measurement

The initial technique to be used to measure viscosity will be that of timing the rate of fall of a dense sphere through a molten sample, with calculation of the viscosity from Stokes' Law. This will require the preparation of small spheres by grinding of suitable materials which are non-reactive in the melts and are of appropriate size and density to produce a sinking rate compatible with the viscosity of the melt and the time scale achievable in the experiments. Noble metals or refractory minerals which are nearly in equilibrium with or slow to dissolve in the melts can be used for the spheres, and the sinking rate can be determined after a known period of time at constant temperature by cooling and sectioning the container to measure the position of one or more spheres [53]. Both viscosity and density of the melt can be determined simultaneously by running experiments containing two or more spheres of different densities [54]. Some in situ method to electrically record the sinking rate or the time for a sphere to sink to the bottom would be an improvement, and attempts will be made to devise such a technique.

The large size of the 4 kbar pressure vessel will readily lend itself to the falling sphere experiments, making possible the use of long tubes of melt and the running of multiple experiments within the chamber simultaneously. Care will be required to insure that the melt within such a cylinder is uniformly saturated in the volatiles of interest; this may require multiple fusions of the lava sample under gas pressure in the apparatus prior to the viscosity experiment. The falling sphere experiments can be duplicated in cylinders of volatile-free melt at atmospheric pressure for comparison with the existing determinations of viscosity of silicate melts.

The viscosity of multiphase silicate melts, containing either suspended crystals or gas bubbles, is of considerable interest. Such measurements are more difficult to make--uniformly controlling the distribution of the suspended phase within the melt is a problem--but they would be of great value, even at atmospheric pressure alone. The dependence of viscosity on shear rate, and the existence of a significant yield strength, are expected to be particularly significant in multiphase systems [55]. Multiphase viscosity measurements will not be a part of the initial set of experiments but will be attempted eventually, first at atmospheric pressure with a rotating-cylinder viscometer and eventually under pressure if, as seems to be possible [56], a rotating viscometer can be adapted to operate within the 4 kbar pressure vessel. The technique of a torsional oscillating piezoelectric crystal has also been used to measure the viscosities of fluids at high temperatures and pressures (to 1200°C and 5 kbar [57]). It should be possible, using the falling sphere method alone, to obtain some data on non-Newtonian effects such as the existence of a yield strength and on changes in the effective sinking rate of crystals when a number of adjacent particles are falling simultaneously through a melt (as is the case in crystal settling in natural magmas).

Electrical Conductivity Measurement

The technique for the conductivity measurements will require either two or four electrodes in the melt, optimally two current-carrying electrodes and, at a closer spacing, two potential-measuring electrodes to avoid polarization effects which can develop at the current electrodes. The arrangement used may be that of several wire electrodes within a crucible, or a conductive crucible itself may serve as one electrode. Several electrodes affixed in a known geometry to a suspended small drop of lava are a very advantageous arrangement because a small drop can equilibrate very rapidly with a surrounding gas atmosphere [58]; it may be possible to use such an arrangement once a rigid chamber is incorporated within the pressure vessel. The conductivity of the sample can either be calculated directly if the electrode geometry is simple, or the electrode geometry can be duplicated and the measurement repeated with a fluid of known conductivity. A General Radio type 1683 automatic RLC bridge is on hand to make electrical measurements and transmit them to the computer in digital form. The 1683 bridge operates at fixed frequencies of 120 and 1000 Hz; these frequencies are suitable for the conductivity

measurements. The high temperature conductivities are expected to be flat with respect to frequency over the approximate range of 1 to 10^4 Hz; an apparent falloff in conductivity is sometimes observed at low frequencies but is attributed to electrode or instrumental effects [59]. The conductivity of partially molten rocks is of particular interest, both for theoretical considerations relating to conductivity in regions of the upper mantle which may contain a small fraction of melt [60], and for the interpretation of the conductivity of near-surface igneous bodies such as the partially crystalline Kilauea Iki lava lake. Likewise of interest are the inflections and dips in the conductivity curve with temperature which have been observed at, and just below, the solidus temperature. Experiments in which a relatively large sample is held at constant temperature for an extended period of time to produce an equilibrium texture of partial melt in a solid matrix would be of particular value in studying conductivity near the solidus temperature. Measurements of the conductivity of solid rock are very dependent on porosity, fractures, and the nature of the fluid or gas which fills the pore spaces [61]; these considerations will not apply to measurements on fully dense molten or partially molten rock samples, but will be of significance to measurements made below the solidus temperature or on samples containing gas bubbles.

Electrical conductivity measurements using the technique of a hanging drop will be done first in the controlled-atmosphere furnace at ambient pressure, for comparison with the existing values in the literature and with those to be obtained in the 4 kbar pressure system.

Materials Compatibility Studies

Compatibility experiments between metals and degassed lavas, gas-saturated lavas and simulated magmatic gases at atmospheric pressure have been conducted at Sandia and others are in progress [62]. Materials being tested include pure elements, stainless steels, nickel- and cobalt-based "superalloys," and some ceramics, carbides, nitrides, etc. The purpose of the tests is to understand corrosion processes involving molten magma and the magmatic gas environment to make it possible to select materials for possible engineering applications involved in drilling into a magma body, and, as the high pressure experimentation progresses, to select materials which can be used as nonre-active containers for multicomponent gas mixtures and gas-saturated melts in the laboratory. Tests at elevated pressure will be carried out first using

sealed tubes containing lava plus volatiles in the cold-seal and the internally heated apparatus. Later, tests will be run with the volatile phase continually replenished within the 4 kbar apparatus using an internal chamber as described earlier. Some anticipated effects of elevated pressure include those due to changes in gas density, diffusion rates and reaction rates; the increased solubility of volatiles in the magma; shift of equilibria with pressure; and increased chemical potentials of species such as S_2 which can, under pressure, exceed the values attainable at atmospheric pressure.

Additional Experiments

The measurements discussed in the preceding pages should constitute a reasonable program of experimentation during the first few years in which the 4 kbar system is operating. There are numerous other properties of magma which are of interest and which could advantageously be measured in the 4 kbar pressure vessel. These include:

- Thermal conductivity and heat transfer

- Sound velocity and attenuation

- Surface tension

- Density, compressibility, and thermal expansion

- Diffusion kinetics

- Kinetics of gas solution and exsolution

- Physical interaction between gases and melts (bubble formation during fluid injection, etc.)

- Production of hydrogen/hydrocarbon "fuels" from magma

Most of the above phenomena have been studied somewhat at atmospheric pressure [63] (and at elevated pressures at ambient or moderate temperatures for solid rocks) but little or not at all with pressurized volatiles in the melts.

Improved density data (especially the coefficient of thermal expansion) would be of particular aid to studies modeling convection in magma [64]; the existing thermal expansion data on molten rocks show considerable scatter [65]. Thermal conductivity measurements would also be of value for studies of the cooling of igneous intrusions; the large size of the Sandia 4 kbar pressure vessel may permit some rather unique experiments involving both convective and conductive heat transfer in relatively large samples. Measurements of the effects of suspended crystals, gas bubbles, pressure, dissolved gases, and wave frequency on the propagation of seismic waves through molten or partially molten rock would be of considerable value to the geophysical studies of lava lakes

and underground magma bodies that are now being conducted [66]. Only a few such laboratory measurements have been made [67] and much of the present interpretation of the seismic properties of partially molten rock must be based on theoretical studies or on measurements in simple systems [68]. Diffusion rates in magma and liquid-vapor kinetic and mechanical properties are of importance in understanding a number of observed or inferred processes in magma, including chemical differentiation and crystallization, chemical transfer by a gas phase, the possible absorption of water from surrounding rocks by a magma, the formation of a gas phase in magma during underground cooling or during eruption, and possible heat extraction methods involving the injection of water into or around a magma body. Only a few experimental studies involving volatile-containing melts have been made that relate to these processes [69]. Finally, the concept of producing fuels by generating reduced gas mixtures containing H_2 , CO , and CH_4 through the interaction of water and carbon-containing additives with magma or hot rock has been demonstrated on a theoretical basis and in an experiment at atmospheric pressure [70] but needs to be carried out under the high pressure conditions that would exist in a real environment.

SUMMARY

Experiments on molten rocks will be carried out at atmospheric pressure, at up to 1 kbar in cold-seal pressure vessels, and to 4 kbar in an internally heated pressure system. Equilibrium melting relations of a basalt, an andesite, and a rhyolite will be determined to provide necessary data at atmospheric pressure and at elevated pressures with water and other volatile components present. The solubilities of volatile components of interest (H_2O , CO_2 , SO_2 / H_2S/S_2 , HCl , HF) will be studied along with the phase equilibria. The first physical properties to be measured will be viscosity (using the falling sphere method) and electrical conductivity, in the presence of some of the above volatile components; the same properties will also be measured at atmospheric pressure for comparison. Some of the viscosity and conductivity measurements will begin as soon as the 4 kbar system is operational and will proceed at the same time as the melting equilibria, gas solubility, and materials compatibility experimentation. A number of additional important physical parameters exist which can be the subject of future experiments.

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