FINAL REPORT

Title of Project: Physical Characterization of Magmatic Liquids

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MASTER

I. INTRODUCTION

The two initial funding periods of this grant were (1) from August 15, 1985 to August 14, 1987 and (2) from August 15, 1987 to August 14, 1989. No-cost extensions were requested and approved to extend the period of grant until February 1992.

Long-range goals of this research project are:

1. Characterization of seismic velocity and attenuation (V_P, V_S, Q_P^{-1}, Q_S^{-1}) and electrical properties of selected Hawaiian and related rocks under appropriate controlled environments of pressure, temperature and volatile/fluid content.

2. Characterization of the elastic, viscoelastic and thermodynamic properties (V_p, V_S, Q_P^{-1}, Q_S^{-1}, viscosity and compressibility) of molten basalts, picrites and komatiites, and related silicate melts to $\sim 1600^\circ$C using the ultrasonic interferometry method. In addition, the pressure dependences of V_P, V_S and bulk modulus (or compressibility) will be determined using the Brillouin scattering and diamond-anvil cell techniques.

II. ACCOMPLISHMENTS

In light of the above-mentioned long-range goals of this research project, we placed emphasis on two important aspects and achieved success:

> (1) Ultrasonic studies of natural and synthetic silicate melts (to 1600°C, or higher)
> (2) Brillouin scattering studies of synthetic silicates and oxides (to 1000°C, or higher, to melting temperatures)

(1) Ultrasonic Studies on Natural and Synthetic Melts

Ultrasonic technique has proven successful in characterizing the elastic and anelastic behavior of natural silicate melts of mainly basaltic composition (eg. Manghnani et al., 1981; Rivers and Carmichael, 1981; Sato and Manghnani, 1985; Rivers, 1985; Kress et al., 1988; Kress and Carmichael, 1990; Secco et al., 1991). These properties must be firmly established at 1 bar in order to provide a basis for the derivation of the high pressure elastic and anelastic behavior of silicate liquids.

The ultrasonic interferometry method (Figure 1) employs two opposed single crystal Mo buffer rods with transducers mounted on the cooled ends. The upper rod is moved up and away from the fixed lower rod, which penetrates through the base of the melt-containing Mo crucible. The transmitted ultrasonic signal, which travels from the upper rod through the melt and lower rod and is sensed by the lower transducer, traces out an alternating constructive (maxima) and destructive (minima) interference pattern as the rod to rod separation (i.e. melt thickness) changes and periodically corresponds to $n\lambda/2$, resonance, and $(n+1/2)\lambda/2$, anti-resonance conditions, respectively, where λ is the ultrasonic wavelength in the melt. The maxima (and minima) separation on a plot of transmitted amplitude versus melt thickness (examples shown in Figure 2) defines $\lambda/2$. Combining this with the known

carrier-wave frequency, the velocity is easily calculated. The attenuation (or inverse quality factor, Q_P^{-1}) is embodied in the decay of the signal amplitude as a function of melt thickness. It is calculated by a least squares fitting of a theoretical interference pattern (derived from wave theory), an adjustable parameter of which is Q_P^{-1}, to the observed amplitude vs. melt thickness data.

Using this technique, measurements of the compressional wave velocity, V_P, and attenuation, Q_P^{-1} have been made in melts of six komatiites, five basalts and three picrites. The komatiites ranged in MgO composition from 13.1 wt % to 29 wt % (see Tables 1 and 2 for ranges of composition of MgO and the liquidus temperatures). The results are discussed and compared in terms of frequency, temperature and compositional (structural) variations.

The 1-bar adiabatic compressibilities, β, and viscosities, η, (which are derived from V_P and Q_P^{-1}) of these ultramafic melts and show the distinctly different behavior between melts with less than and melts with greater than ~ 22 wt % MgO. The results have been interpreted in terms of the compositionally controlled melt structure. Ultrasonic velocity (V_p) and attenuation (Q_p^{-1}) data for various natural and synthetic silicate melts have also provided useful constraints on the viscosity and bulk modulus (K_S) of magmatic liquids at ambient pressure, whereas the static compression and shock wave studies have thrown new light on the densification of magmatic liquids at mantle pressure.

The two most important features of the properties of komatiite melts are: (1) its bulk modulus increases with MgO content; and (2) as a result of their relatively more depolymerized nature, the Q_p values are much higher (400-800), as compared to those for basaltic and picritic melts (40-80), and there is virtually no dispersion in velocity and attenuation in wide ranges of temperature.

The viscosities and their activation energies of the silicate melts increase with the basicity and polymerization of the melt. Using the ultrasonic results and the measured values of shear viscosity (η_S) and volume viscosity (η_V), the structural relaxation times (τ) are deduced and corroborated. In sum, the composition and structure (nonbridging oxygens per tetrahedrally coordinated cation (NBO/T)) play important roles in the viscoelastic properties of silicate melts.

(2) Brillouin Scattering Studies of Synthetic Silicates and Oxides

Brillouin scattering is a powerful geophysical tool (Anderson et al., 1967). The phenomenon of Brillouin scattering may be described as either a classical Bragg reflection from the wavefronts of thermally generated plane waves, or as a quantum-mechanical phonon-phonon interaction. The Brillouin spectrum of light scattered from liquid contained in a crucible inside the furnace consists of a central unshifted line (Rayleigh) and two pairs of peaks (Brillouin) symmetrically shifted from the central line. The hypersonic velocity can be determined from the well known equation (Brillouin, 1922)

$$\triangle \nu = 2 \frac{nV}{c} \nu_o \sin \frac{\theta}{2}$$

where $\Delta\nu$ is the measured shift (Doppler effect) in frequency, n is the index of refraction, V is the velocity of sound in liquids, c is the speed of light, and θ is the scattering angle. A measurement of the scattering angle and the shift $\Delta\nu$ allows a direct calculation of elastic wave velocity. The Brillouin line shape is related to the time decay of the acoustic wave in the medium. The height of the Brillouin line will give the spatial attenuation coefficient (α_v) according to

$$\omega_h = \frac{\alpha_v V}{2}$$

where V is the elastic velocity. The main advantages and potential uses of Brillouin scattering technique for studying melts are: (i) it is a proven technique which complements the ultrasonic measurements; (ii) temperature limit is not controlled by transducer properties; (iii) measurements at simultaneously high pressure and temperature (in a diamond-anvil cell) are feasible; and (iv) in contrast to ultrasonic method, V_S can be measured in a melt more easily. In an effort to establish the composition-structure-property relationships for silicate liquids, we have successfully determined various elastic, thermodynamic and structural properties of silicate glasses (through melting temperatures) and of melts by combined use of the Brillouin and Raman scattering techniques. By employing zirconia (ZrO_2) anvils in the diamond-anvil pressure cell, we successfully carried out a feasibility study of the compressibility of silicate melts under high pressure.

III. RESULTS AND PUBLICATIONS

Excellent progress was made during the grant period (August 15, 1985-February 1992) to accomplish the goals of research. The important results are summarized below:

- The linear Birch V_P-ρ relationship holds well for basaltic, picritic and komatiitic melts (Figure 3).

- Figue 4 shows that bulk modulus ($K=1/\beta$) of basic and ultrabasic melts systematically increases with depolymerization (large NBO/T values). In other words, the compressibilities (β) of these melts decrease systematically with melt depolymerization. In the komatiitic melts studied, the high-MgO ($\geq \sim 22$ wt% MgO) melts are ~ 15 % less compressible than the low-MgO melts. In terms of their MgO wt % (w), $d\beta/dw_{highMgO} \approx 4d\beta/dw_{lowMgO}$.

- The larger proportion of chain (TO_3) and monomeric (TO_4) units relative to the 3-d network (TO_2) units in the depolymerized (large NBO/T) values) high-MgO melts results in lower molar volume. In addition, since Al-O bonds are weaker than Si-O bonds, a lower Al/(Al+Si) ratio for the high MgO melts combined with their lower molar volumes accounts for their lower compressibilities.

- Bond severance required for viscous flow is facilitated by depolymerization due to the larger proportion of TO_3 and TO_4 units (whose non-bridging bonds are weaker than the T-O-T bridging bonds of the TO_2 (fully polymerized units). The viscosities of the komatiitic

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melts (determined from ultrasonic measurements) follow Arrhenius behavior (Figure 5) with activation energies for viscous flow, E_n, of approximately 285 kJ/mol.

- Temperature dependences of V_P, V_S and bulk modulus of silicate glasses and their melts have been determined by Brillouin scattering using a high-temperature (up to 1000°C) furnace (see appended papers 7 and 8). We have recently acquired another furnace from Centorr which allows us to study the silicate glasses and melts up to 2000°C.

Seven published papers resulting out of this research are:

1. Sato, H. and M. H. Manghnani, Ultrasonic measurements of V_P and Q_P: Relaxation spectrum of complex modulus on basalt melts, *Phys. Earth Plan. Int.* **41** , 18-33, 1985.

2. Sato, H., M. H. Manghnani, B. R. Lienert and A. T. Weiner, Effects of sample-electrode interface polarization on the electrical properties of partially molten rocks, *J. Geophys. Res.* **91 B** (9), 9325-9332, 1986.

3. Manghnani, M. H., H. Sato and C. S. Rai, Ultrasonic velocity and attenuation measurements to 1500°C: Role of composition and structure in the viscoelastic properties, *J. Geophys. Res.* **91 B** (9), 9333-9342, 1986.

4. Weiner, A. T., M. H. Manghnani amd R. Raj, Internal friction of Tholeiitic Basalts, *J. Geophys. Res.* **92** 11,635-11,643, 1987.

5. Secco, R. A. , M. H. Manghnai and T. C. Liu, Bulk modulus-attenuation-viscosity systematics of diopside-anorthite melts, *Geophys. Res. Lett.,* **18,** 93-96, 1991.

6. Secco, R. A. , M. H. Manghnani and T. C. Liu, Velocities and compressibilities of komatiitic melts, *Geophys. Res. Lett.,* **18,** 1379-1400, 1991.

7. Xu, Ji-an and M. H. Manghnani, Brillouin scattering studies of a sodium silicate glass in solid and melt conditions at temperatures of up to 1000°C, *Phys. Rev. B,* **45,** 640-645, 1992.

In addition, two papers have been submitted for publication:

8. Xu, Ji-an, and M. H. Manghnani, Brillouin scattering studies of $K_2Si_4O_9$ glass and melt up to 1000°C, *Phys. Rev. B* (submitted).

9. Askarpour, V., M. H. Manghnani, S. Fassbender and A. Yoneda, Elasticity of single-crystal $MgAl_2O_4$ spinel up to 1273 K by Brillouin spectroscopy *Phys. and Chem. of Miner.* (submitted).

10. Manghnani, M. H., R. A. Secco, Elastic and viscoelastic properties of silicate melts: A review, International Geological Congress, 1992 (in preparation).

The abstract of a review paper on the viscoelastic properties of magmatic liquids, (in preparation) is appended.

IV. GRADUATE STUDENT THESIS

Weiner, Adam T., Electrical Conductivity and Internal Friction in Basalts, M. S. degree, University of Hawaii, 85 p., 1986.

V. BIBLIOGRAPHY

Kress, V. S., Q. Williams, and I. S. E. Charmichael, Ultrasonic investigation of melts in the system Na_2O-Al_2O_3-SiO_2, *Geochim. et Cosmochim. Acta,* **52**, 283-293, 1988.

Manghnani, M. H., C. S. Rai, K. W. Katahara, and G. R. Olhoeft, Ultrasonic velocity and attenuation in basalt melt, in *Evolution of the Earth Geodyn. Ser.,* vol. 5, edited by R. J. O'Connell and W. S. Fyfe, pp. 118-122, AGU, Washington, D. C., 1981.

Manghnani, M. H., H. Sato, and C. S. Rai, Ultrasonic velocity and attenuation measurements on basalt melts to 1500°C: Role of composition and structure in the viscoelastic properties, *J. geophys. Res.,* **91**, 9333-9342, 1986.

Rivers, M. L. and I. S. E. Charmichael, Ultrasonic studies of silicate melts, *J. Geophys. Res.,* **92**, 9247-9270, 1987.

Sato, H., M. H. Manghnani, Ultrasonic measurements of V and Q: Relaxation spectrum of complex modulus on basalt melts, *Phys. Earth Planet. Inter,* **41**, 18-33, 1985.
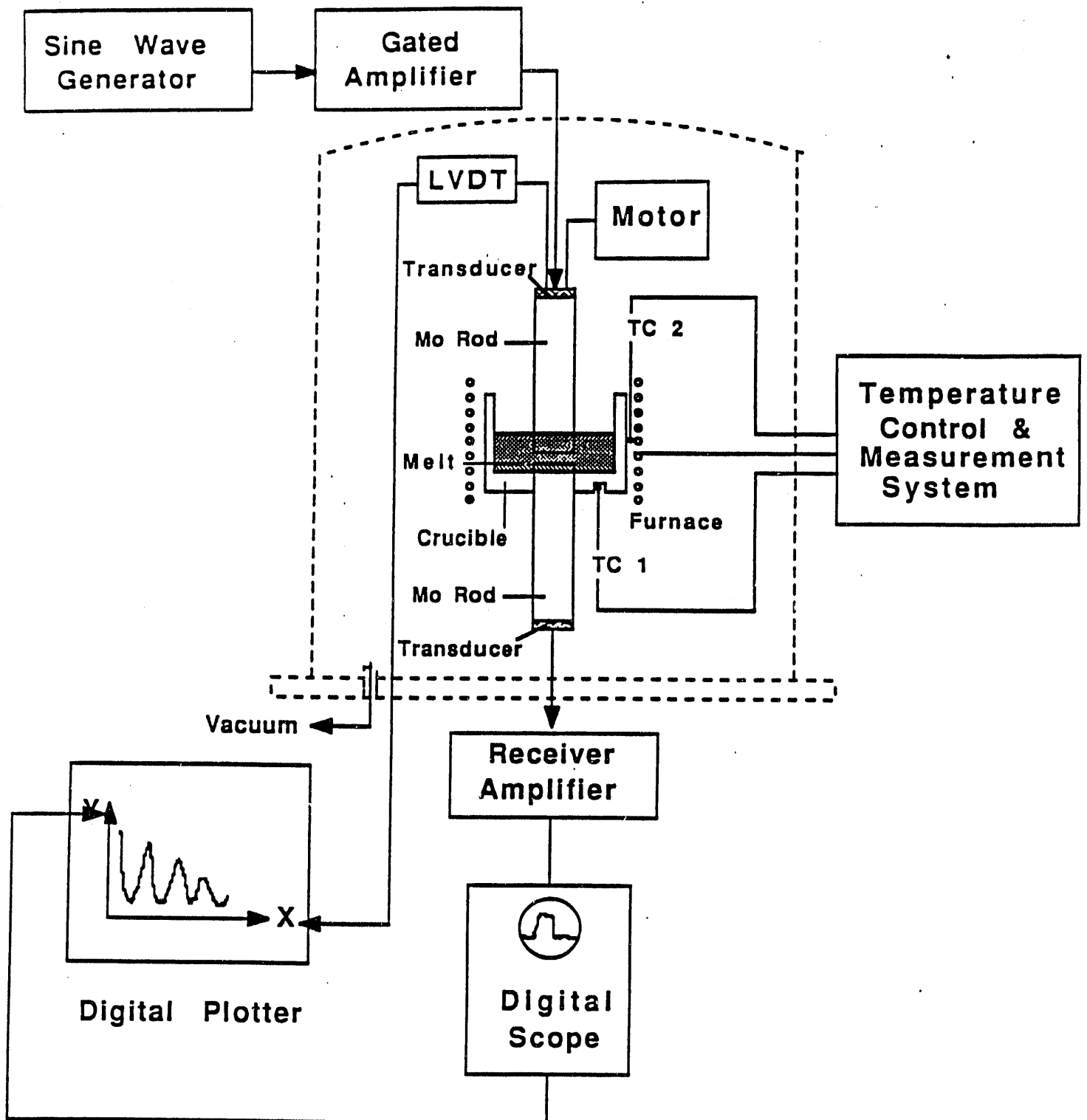
Figure 1. Schematic diagram of apparatus for measuring melt velocity and attenuation by ultrasonic interferometry.
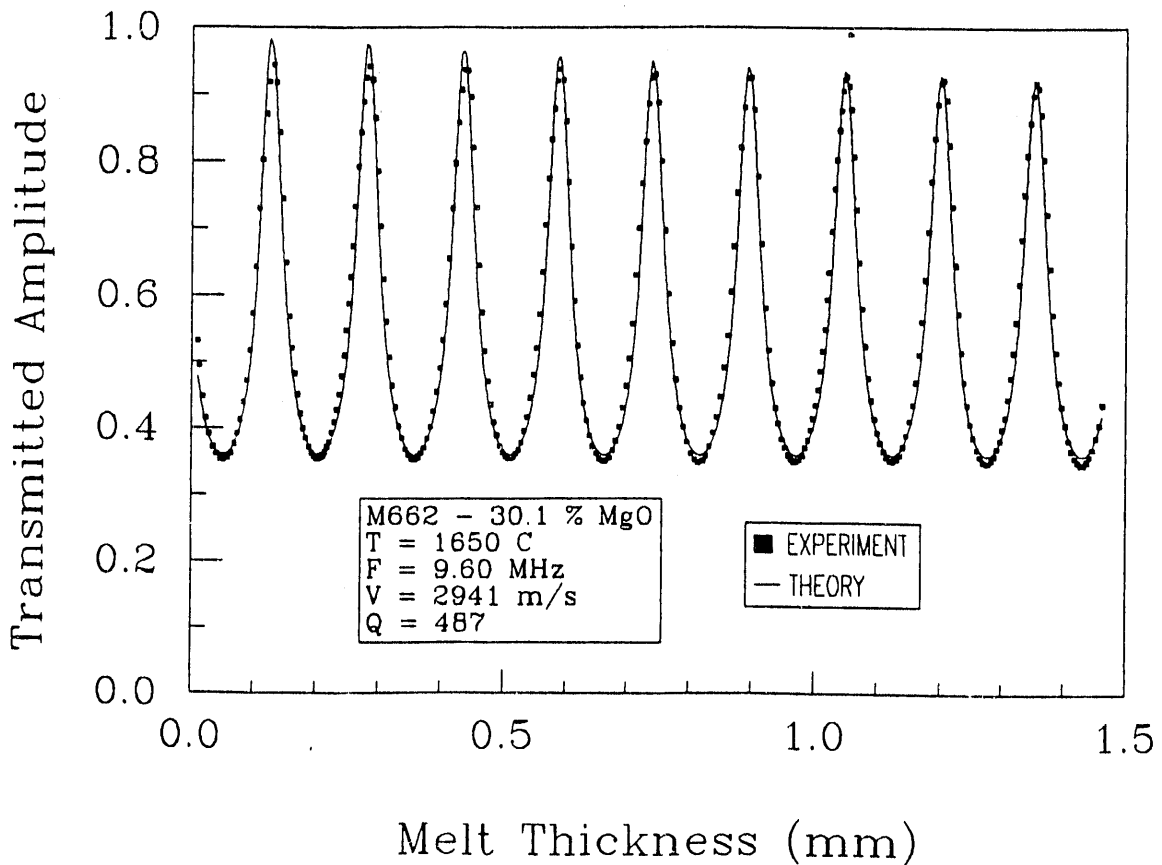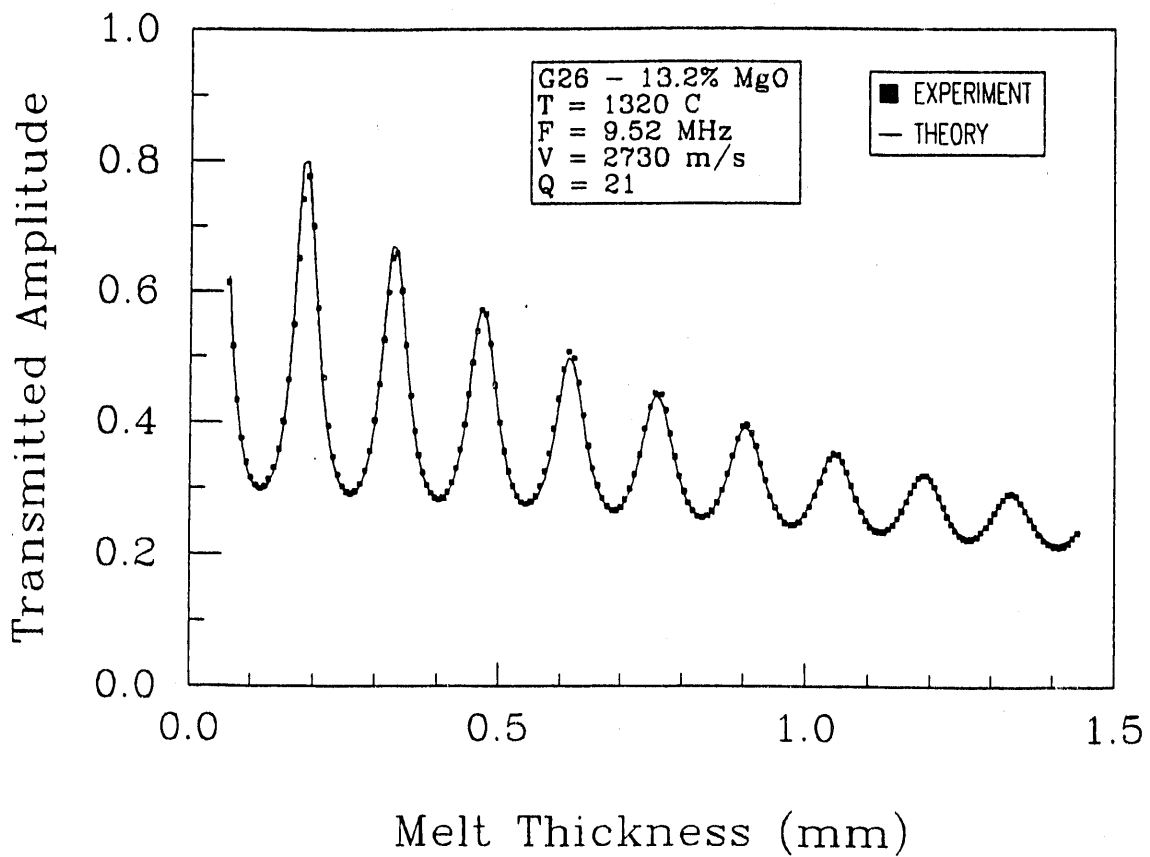
Figure 2. Interferogram of measured transmitted amplitude of an 9.52 MHz p-wave as a function of melt thickness (komatiite G26) at 1320°C (upper plot); and 9.60 MHz interferogram (komatiite 662) at 1650°C. Note different Q values for the two melts.
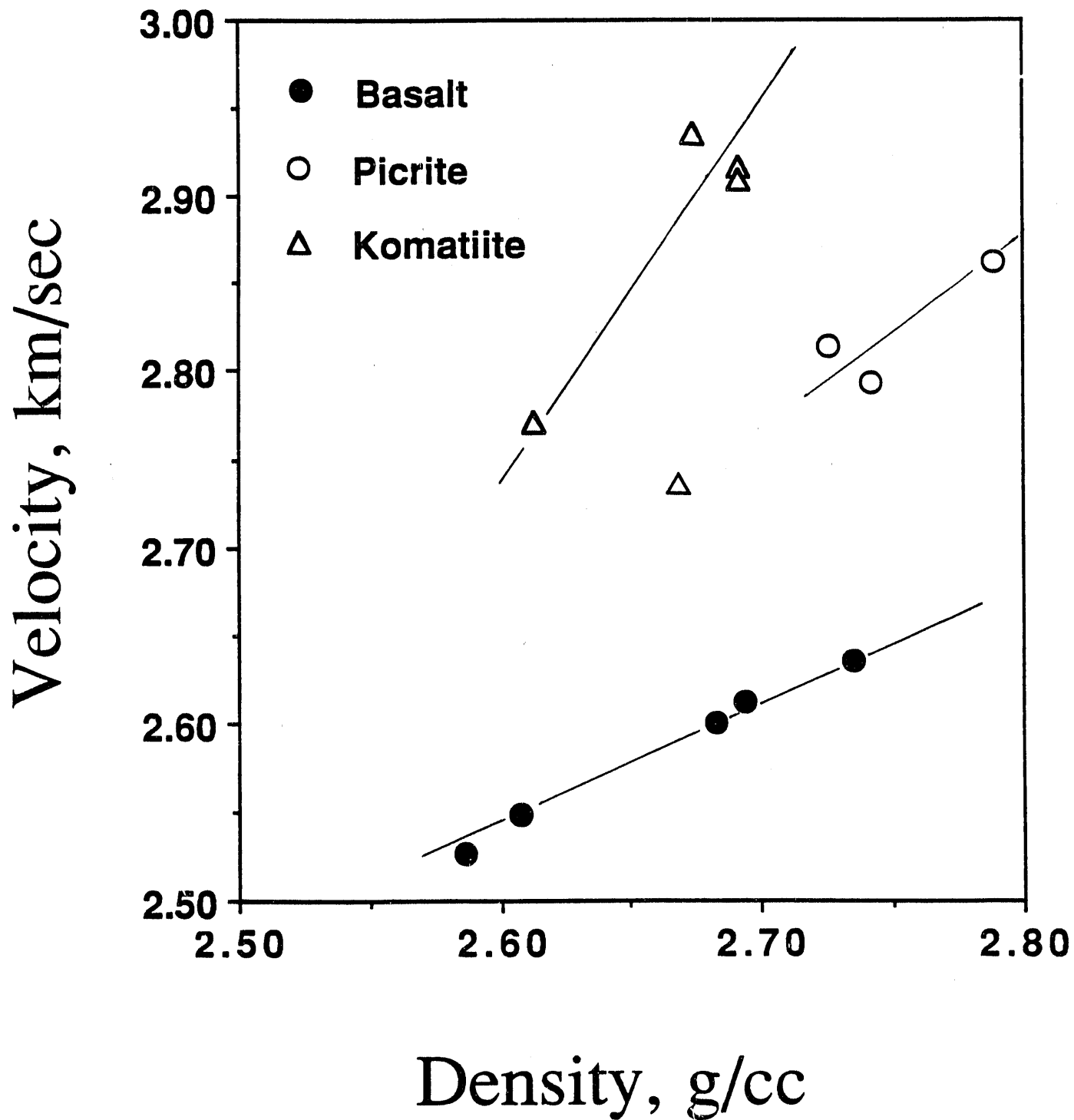
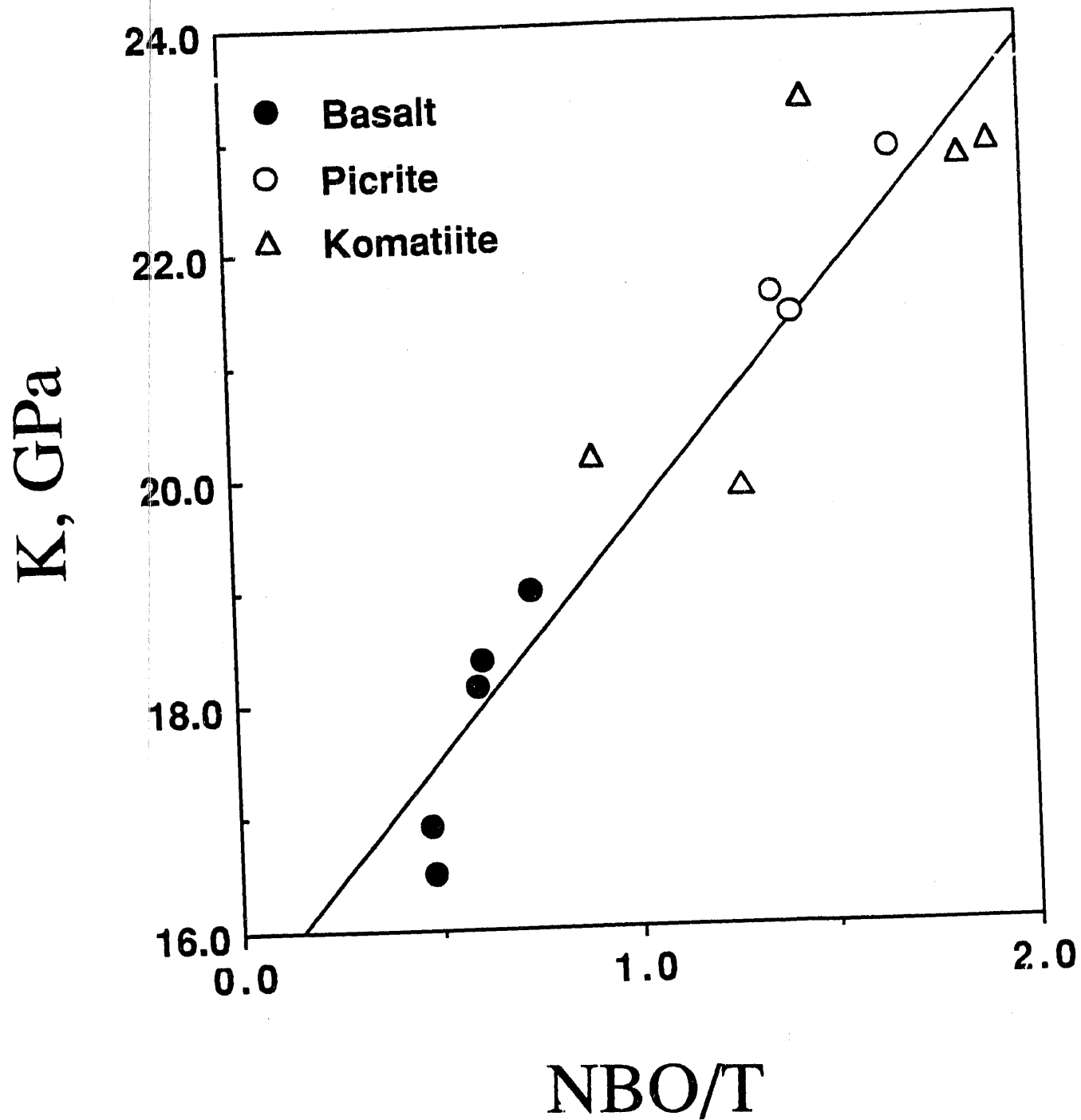Figure 3. Linear V_P-ρ Birch relationship for basaltic, picritic, and komatiitic melts.

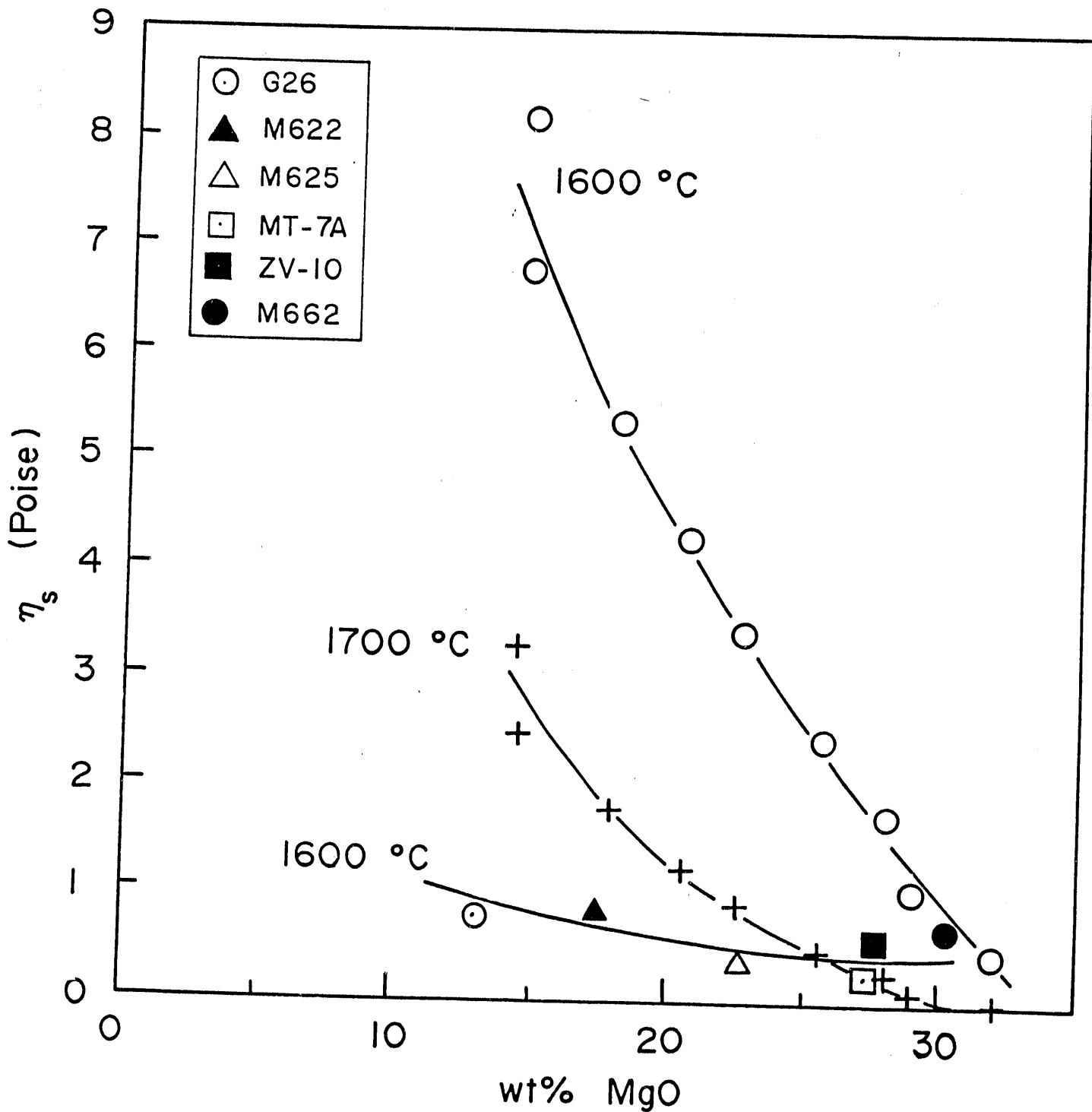Figure 4. Bulk modulus versus NBO/T for basaltic, picritic and komatiitic melts.

Figure 5. Shear viscosities, η_s, of Belingwe lavas at 1600°C (O) and 1700°C (+) calculated with the Bottinga and Weill (1972) viscosity model (from Nisbet, 1982). The remaining data are η_s values for the komatiites in this study calculated from $\eta_l = \rho V_p^2/\omega Q_p$ (assuming $\eta_s = 3\eta_l/7$; Sato and Manghnani, 1985; Dingwell and Webb, 1989) using ultrasonic measurements of V_p and Q_p at 5 MHz.

TABLE 1. Komatiite compositions* (wt%), liquidus temperatures
and NBO/T values.

Oxide	M662	ZV–10	MT–7A	M625	M622	G26
SiO_2	45.76	47.41	46.14	46.07	50.96	49.45
TiO_2	0.32	0.30	0.36	0.46	0.50	0.83
Al_2O_3	6.40	6.36	7.63	9.44	10.27	11.40
FeO**	10.52	10.70	9.68	11.60	8.97	11.50
MnO	0.16	0.18	0.07			
MgO	30.10	27.46	27.24	22.73	17.42	13.22
CaO	6.20	6.71	7.39	9.13	10.07	11.40
Na_2O	0.44	0.82	0.87		1.54	2.10
K_2O	0.10	0.04	0.22	0.05		0.10
P_2O_5		0.02				
Cr_2O_3			0.40	0.42	0.27	
NiO				0.10		
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00
$T_{liq}(°C)$	1600	1552	1548	1448	1350	1290
NBO/T**	2.14	1.97	1.92	1.67	1.25	1.16

* Normalized to 100 wt% without volatiles.
** Total Fe as FeO.

Table 2. MgO content and calculated [Nisbet and Arndt, 1982]
liquidus temperatures of komatiites used in the present study

Sample	MgO (wt. %)	Liquidus Temp.	Temp. range of measurements
G26	13.1	1290°C (1563K)	1280-1500°C
M622	17.3	1350°C (1623K)	1350-1600°C
M625	22.4	1450°C (1723K)	1450 1530°C
ZV10	26.21	1522°C (1795K)	1496-1661°C
MT-7A	27.24	1535°C (1808K)	1507-1661°C
M662	29.60	1595°C (1868K)	1475-1650°C

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