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Stishovite: A Comparison of Shock Compression Data with Static Compression and Ultrasonic Data

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ABSTRACT

The ultrasonic and static compression data for stishovite were transformed to shock and particle velocities and compared with the higher pressure shock compression data for α-quartz. Using the transformation scheme described in the text, good agreement is found between the shock data and stishovite zero pressure moduli ranging from $K_o = 300$ GPa, $K_o' = 3$ to $K_o = 250$ GPa, $K_o' = 6$.

There is interest in the equation of state of stishovite, the stable solid phase of SiO_2 at some pressure above 8 GPa (80 kilobars), because there is substantial evidence showing that silicates decompose to oxide states at conditions inside the earth; a major constituent of these oxides is SiO_2. Data has been gathered on stishovite at earth-interior conditions using shock compression techniques, [Wackerle, 1962], [Altshuler et al., 1965], [Trunin et al., 1970], [Trunin et al., 1971], but the results are complicated by having to start with materials, such as α-quartz or glass, from which the stishovite phase is obtained under shock compression only after undergoing a phase transformation involving large energy and volume changes.

More recently there has been substantial work on the thermodynamic properties of pure stishovite. The heat capacities and enthalpies of transformation were determined by Holm et al. [1967] for glass, α-quartz, and stishovite. Also, there have been two determinations of the volume thermal expansion [Weaver et al., 1973], [Ito et al., 1974]. And finally, determinations of the zero pressure bulk modulus $(V_0 \partial P/\partial V)_{P = 0}$ have been made using ultrasonic techniques [Mizutani et al., 1972], [Chung, 1974], [Liebermann et al., private communication 1976] and using high pressure x-ray diffraction techniques [Bassett and Barnett, 1970], [Liu et al., 1974], [Olinger, 1976a]. Here the bulk modulus determinations will be compared to the shock compression data using the heat capacity, transformation enthalpy, and thermal expansion data.

The isothermal compression is first described in terms of the linear shock-particle velocity equation analog introduced by Olinger and Halleck [1975]. The analog relations are

$$U_{st} = c_t + s_t U_{pt}, \tag{1}$$

$$U_{st} = (PV_o/(1-V/V_o))^{1/2}, \tag{2}$$

$$U_{pt} = (PV_o\ (1-V/V_o))^{1/2}, \tag{3}$$

$$V/V_o = (U_{st}-U_{pt})/U_{st}, \tag{4}$$

$$P = U_{st}U_{pt}/V_o, \tag{5}$$

where V_o is the specific volume at ambient conditions and V is the specific volume at pressure P. The compatible units to use in equation (1) through (5) are P in GPa, V in cm^3/g, and U_{st}, U_{pt} in km/s. For those more accustomed to the familiar Murnaghan and Birch-Murnaghan P-V equations, the isothermal zero pressure bulk modulus from Eq. (1) is

$$K_{ot} = c_t^2/V_o, \tag{6}$$

and its pressure derivative is

$$K'_{ot} = 4\ s_t-1. \tag{7}$$

For the pressure range covered here for stishovite, 200 GPa or 2 megabars, the three equations of state are nearly interchangeable. The P,V conditions along the shock compression locus are described by equations identical to Eqs. (1) through (5) except that U_{st} becomes U_s, the shock velocity, and U_{pt} becomes U_p, the mass or particle velocity. Also in Eqs. (6) and (7), the expressions are equated to adiabatic moduli instead of isothermal moduli.

The pressure, P_t, associated with a given volume, V_L, along the isothermal compression curve of stishovite is transformed to the pressure, P_h, along the shock compression Hugoniot associated with the same volume by the following expression [Olinger et al., 1975].

$$P_h\{V_L\} = \frac{P_t\{V_L\}\ V/\gamma + \int_{V_o}^{V_L} P_t dV - [T\gamma/V\ C_v]\ (V_L - V_o)}{[V/\gamma - 1/2\ (V_o - V_L)]}. \quad (8)$$

where γ is the Grüneisen constant

$$\gamma = \alpha_v c_s^2/C_p. \quad (9)$$

In the above equations T is the ambient temperature (293° K), C_v and C_p are the specific heat capacities at constant volume and pressure and c_s is the adiabatic bulk sound speed. C_v and c_s or c_t can be calculated from C_p and c_t or c_s or vice-versa using the following relations,

$$C_v = C_p - \alpha_v^2\ T\ c_t^2, \quad (10)$$

$$c_t = c_s\ \left(\frac{C_v}{C_p}\right)^{1/2}, \quad (11)$$

where α_v is the volume thermal expansion.

The integral in Eq. (8) can be determined by several methods. Here it was done using numerical integration.

$$\int_{V_o}^{V_L} P_t\ dV = \sum_{r=1}^{L} \frac{P_{tr} - P_{tr-1}}{2}\ (V_r - V_{r-1}), \quad (12)$$

where

$$V_r = V_o\ (U_{str} - U_{ptr})/U_{str}, \quad (13)$$

and

$$P_{tr} = (1/V_o)\ U_{str}\ U_{ptr}. \quad (14)$$

In Eq. (8) both (γ/V) and C_v are assumed to remain constant [McQueen et al., 1967].

Once the P,V conditions have been defined along the Hugoniot starting with crystal density stishovite (from Eq. 8), then new pressure values can be calculated for stishovite at the given volume, V_L, to account for the energy increase resulting from the transformation from α-quartz under shock compression. The transformation equation was described earlier [McQueen et al., 1963], [McQueen et al., 1967]

$$P_h' \{V_L\} = \frac{P_h\{V_L\}[1 - (\gamma/V)(V_{os} - V_L)/2] + (\gamma/V)[\Delta E_o]}{1-(\gamma/V)(V_{oQ} - V_L)/2}, \qquad (15)$$

where V_{os} is the ambient specific volume of stishovite, V_{oQ} is the ambient specific volume of quartz, and ΔE_o is the ambient internal energy difference between α-quartz and stishovite. Once the P_h', V_L values for stishovite have been calculated, they then can be transformed into U_s, U_p values having α-quartz for the starting material,

$$U_s = (P_h' V_{oQ}/(1-V_L/V_{oQ}))^{1/2}, \qquad (16)$$

$$U_p = (P_h' V_{oQ}(1-V_L/V_{oQ}))^{1/2}, \qquad (17)$$

and compared directly to the shock compression data. The three thermodynamic quantities independent of the ultrasonic and high pressure x-ray studies are ΔE_o (822.1 J/g [Holm et al., 1967]), C_p (0.704 J/g K° [Holm et al., 1967]), and α_v (13.1×10^{-6}/K° [Ito et al., 1974]). The thermal expansion of Ito et al. [1974] was chosen instead of the value from Weaver et al. [1973] because more information was available about the experimental technique used by the former, and the experiment appeared to be carefully done.

The U_s, U_p shock compression data for stishovite transformed from near crystal density α-quartz are listed in Table I with their sources. As can be seen in the table, the data credited to Altshuler et al. [1965] are repeated by Trunin et al. [1970]. Whether they are independent data or the same is not indicated by Trunin et al. [1970].

The results of the comparisons of the various compression data and ultrasonic data with the shock data are summarized in Fig. 1. The data listed in Table I are plotted there along with the calculated Hugoniot of α-quartz based on a hydrostatic compression study by Olinger [1976b]. The bulk modulus, its pressure derivative, and the Grüneisen constant used for each calculated curve are listed in Table 2. Curves a, b, and c are taken from the data of Olinger [1967a] plotted in Fig. 2. Most confidence was placed on a selected, average datum, $V/V_o = 0.9674 \pm 0.0008$, $P = 10.58 \pm 0.14$ GPa. For curve a the U_s,U_p slope was adjusted so $K_o' = 6$ and yet the curve would pass through the averaged datum. The value of 6 was chosen for the zero pressure, pressure derivative of the bulk modulus because that was the average value of the derivative of the modulus for similarly structured solids, TiO_2, SnO_2, and GeO_2. The resulting bulk modulus is 288 GPa. As shown in Fig. 1, curve a passes through the lower U_s,U_p data but misses the high pressure (200 GPa or 2 megabar) data of Altshuler et al. [1965] and Trunin et al. [1970].

Two other fits to the data of Olinger [1976a] were therefore tried. Curve b was chosen because it gave a good fit to the shock compression data and passed through the selected datum ($K_o = 304$ GPa, $K_o' = 3$ GPa). Curve c was based on a linear least squares fit to all the data from Olinger [1976a] ($K_o = 314$ GPa, $K_o' = -0.4$). Again, the curve passes through the lower pressure U_s,U_p data but misses the high pressure data. These three curves, a, b, and c, can equally well represent the results of Bassett and Barnett [1970] and Chung [1974] where the bulk modulus was found to be approximately 300 GPa.

Both Mizutani et al. [1972] and Liu et al. [1974] determined the bulk modulus of stishovite to be 345 GPa. Curves d and e represent stishovite having a moduli of 350 GPa and a pressure derivative of the modulus of 6 and 3 respectively. Obviously the curves miss the U_s,U_p data entirely. Finally, Liebermann et al. [private communication 1976] determined a bulk modulus of 250 GPa for stishovite and selected the pressure derivative of 6 as others have done. Curve f represents his results and that curve agrees as well with the U_sU_p data as does curve b. (Both curve b and f are shown here as one curve.) In summary, based on the calculation scheme used here, and more important, based on the assumption the very high pressure U_s,U_p data is correct (in the 200 GPa region), the presently available U_s,U_p data is consistant with a spectrum of experimental static data for pure stishovite ranging from K_o = 300 GPa, K_o' = 3 to K_o = 250, K_o' = 6. Should it turn out that the three highest pressure shock data considered here are for SiO_2 in the liquid state, a possibility discussed by Trunin [1970], the metastable stishovite in the U_p range of 6.2 km/s would have higher U_s values than the 12.01 to 12.12 km/s listed for the data in Table 1. This would, in turn, alter the conclusions here by suggesting that the pressure differential of the bulk modulus would be greater than 3 for a modulus of 300 GPa.

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BIBLIOGRAPHY

Altshuler, L. V., and R. F. Trunin, and G. V. Simakov, Shock compression of periclase and quartz and the composition of the lower mantle, Izv. Acad. Sci. USSR, Phys. Solid Earth, 10, Engl. Transl., 657-660, 1965.

Bassett, W. A. and J. D. Barnett, Isothermal compression of stishovite and coesite up to 85 kilobars at room temperature by x-ray diffraction, Phys. Earth Planet. Interiors, 3, 54-60, 1970.

Chung, D. H., General relationship among sound speeds, Phys. Earth Planet. Inter., 8, 113-120, 1974.

Holm, J. L., O. J. Kleppa, and E. F. Westrum, Jr., Thermodynamics of polymorphic transformations in silica. Thermal properties from 5 to 1070 K and pressure-temperature stability fields for coesite and stishovite, Geochim. Cosmochim. Acta 31, 2289-2307, 1967.

Ito, H., K. Kawada, and S. I. Akimoto, Thermal expansion of stishovite Phys. Earth Planet. Interiors, 8, 277-281, 1974.

Liu, L., W. A. Bassett, and T. Takahashi, Effect of pressure on the lattice parameters of stishovite, J. Geophys. Res., 74, 4317-4328, 1969.

McQueen, R. G., J. N. Fritz, and S. P. Marsh, On the equation of state of stishovite, J. Geophys. Res., 68, 2319-2322, 1963.

McQueen, R. G., S. P. Marsh, and J. N. Fritz, Hugoniot equation of state of twelve rocks, J. Geophys. Res., 72, 4999-5036, 1967.

Mitzutani, H., Y. Hamano, and S. Akimoto, Elastic-wave velocities of polycrystalline stishovite, J. Geophys. Res., 77, 3744-3749, 1972.

Olinger, B., The compression of stishovite, submitted to J. Geophys. Res., 1976a.

Olinger, B., The compression of α-quartz, submitted to J. Geophys. Res., 1976b.

Olinger, B. and P. M. Halleck, Compression and bonding of ice VII and an empirical linear expression for the isothermal compression of solids, J. Chem. Phys., 62, 94-99, 1975.

Olinger, B., P. M. Halleck, and H. H. Cady, The isothermal linear and volume compression of pentaerythritol tetranitrate (PETN) to 10 GPa (100 Kbars) and the calculated shock compression, J. Chem. Phys., 62, 4480-4483, 1975.

Trunin, R. F., M. A. Podurets, and G. V. Simakov, Compression of porous quartz by strong shock waves, Izv. Acad. Sci. USSR, Phys. Solid Earth, Engl. Transl. 1, 8-12, 1970.

Trunin, R. F., G. V. Simakov, M. A. Podurets, B. N. Moeseyev, and L. V. Popov, Dynamic compressibility of quartz and quartzite at high pressure, Izv. Acad. Sci. USSR, Phys. Solid Earth, Engl. Transl. 2, 102-106, 1971.

Wackerle, J., Shock-wave compression of quartz, J. Applied Phys. 33, 922-937, 1962.

Weaver, J. S., T. Takahashi, W. A. Bassett, Thermal expansion of stishovite, EOS (Trans. Am. Geophys. Union), 54, 475, 1973.

TABLE I. Stishovite U_s,U_p Hugoniot Data Between $U_p = 2.5$ to 6.5 km/s Centered on Near Crystal Density α-Quartz at Ambient Conditions

Wackerle [1962]		Altshuler et al. [1965]	
U_p(km/s)	U_s(km/s)	U_p(km/s)	U_s(km/s)
2.55	6.12	3.13	7.18
2.70	6.29	3.92	8.54
2.89	6.66	6.20	12.01
2.89	6.66	Trunin et al. [1970]	
3.03	6.95	2.52	6.27
3.03	6.95	2.54	6.10
3.42	7.76	3.13	7.18*
3.49	7.76	3.91	8.56
3.50	7.63	3.92	8.54*
3.50	7.72	6.18	12.12
3.52	7.70	6.20	12.01*
3.52	7.75		

*These data may be the same data published in Altshuler et al. [1965]. However, Trunin et al. [1970] does not indicate they are from the former. They are considered here to be from 2 different experiments.

TABLE II. The Bulk Moduli, Their Pressure Derivatives, and Associated Grüneisen Constants Used to Calculate the Curves in Figure 1.

Curve	K_o (GPa)	K'_o	γ
a	288	6	1.26
b	304	3	1.33
c	314	-.4	1.37
d	350	6	1.53
e	350	3	1.53
f	250	6	1.08

FIGURE CAPTIONS

Figure 1. The circles, diamonds, and squares are the shock compression data of SiO_2 with α-quartz as the starting material from Wackerle [1962], Trunin et al. [1970], and Altshuler et al. [1965], respectively. The short curve on the left side is the calculated Hugoniot of the α-quartz phase of SiO_2 [Olinger, 1976b]. Curves a-f are the calculated Hugoniots of stishovite centered on α-quartz at ambient conditions. The stishovite represented by each curve has a zero pressure bulk modulus, a modulus pressure derivative, and a Grüneisen constant associated with it as listed in Table II. The datum shown with vertical error bars is from the static work of Olinger [1976].

Figure 2. The date from Olinger [1976a]. Linear fits a, b, and c are transformed to Hugoniots centered on α-quartz at ambient conditions shown in Fig. 1. The bulk modulus, its pressure derivative, and the Gruneisen constant associated with each fit are listed in Table II.

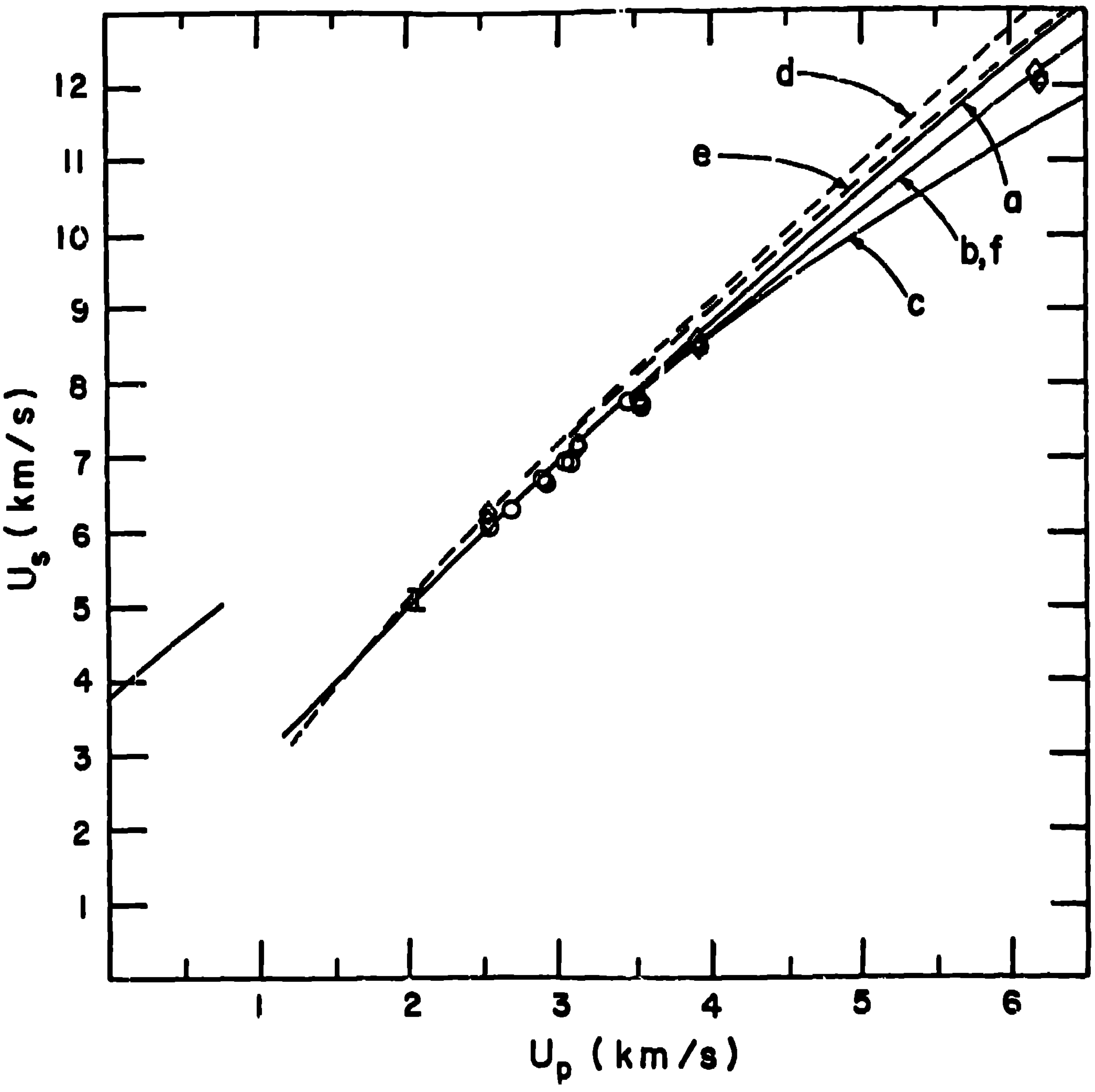

Figure 1

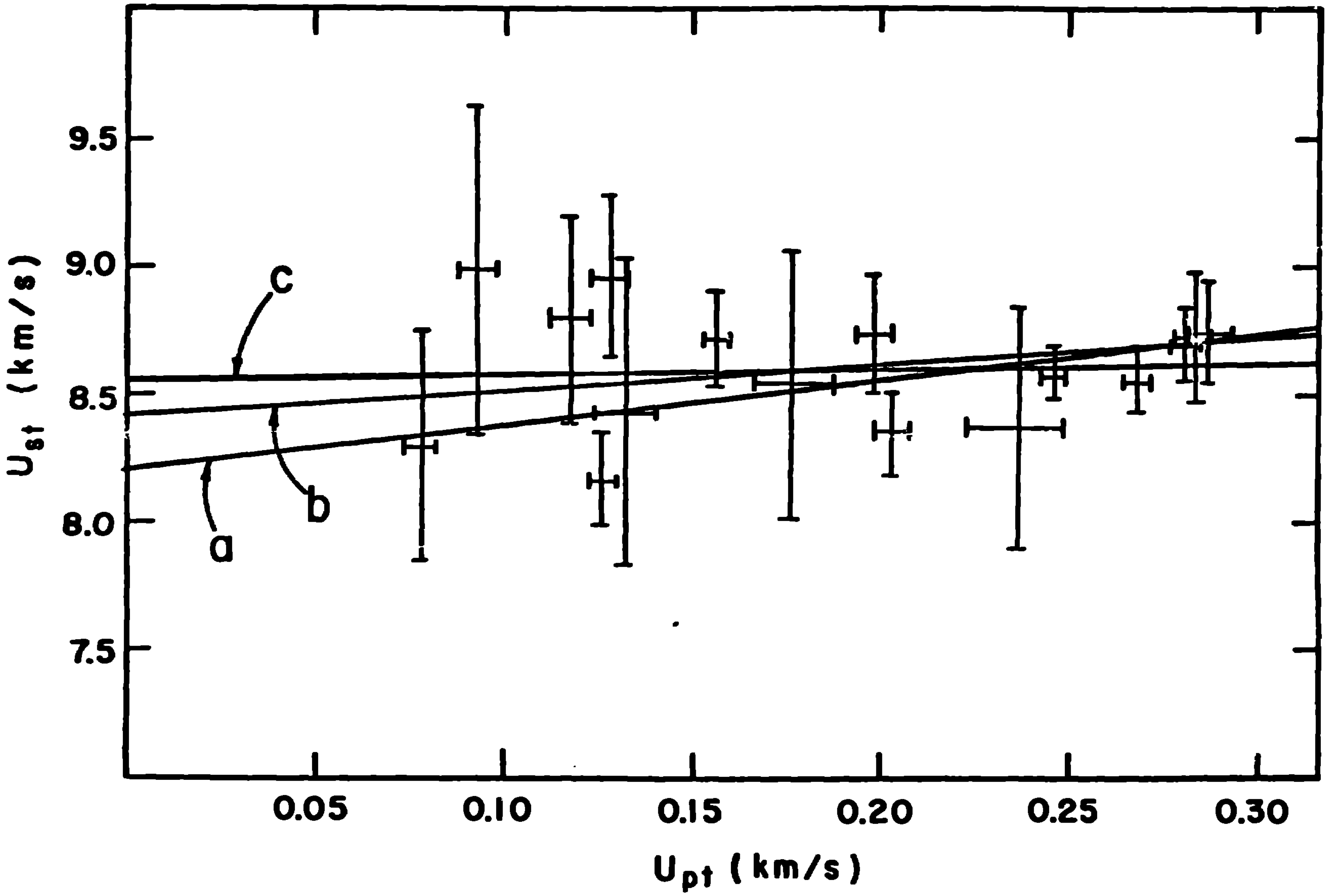

Figure 2