

Senior Thesis

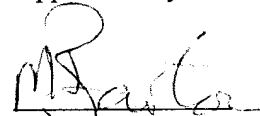
AN ESTIMATE OF P, T, AND WATER CONTENT FOR A LAVA
FROM SANTORINI AND THERMODYNAMIC APPLICATIONS

Presented in Partial Fulfillment of the Requirements for
the Degree of Bachelor of Science in the
Department of Geological Sciences

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Introduction

During the past few years, much work has been done to try to put together internally consistent thermodynamic data sets. As more and more data has come out, it has become increasingly possible to do accurate geothermometry and geobarometry. As is shown in Figure 1, the calculated equilibrium of monticellite, quartz, and fayalite (Berman 1988) matches the experimental data (Haas; Myers & Eugster) almost perfectly. Berman's data set is applicable mainly to metamorphic rocks, but with a few modifications, it may also be used in calculations on igneous rocks.

Now that more accurate data sets are available, it is possible to estimate the pressure, temperature, and water content at which crystallization of a magma occurred with some confidence. There are several reasons why it is important to determine these three conditions. If one is at all concerned with the evolution of magmas, the pressure is important because the depth at which the crystallization begins determines what minerals will be present, and thus the type of rock. Temperature of crystallization can further constrain geochemical models. A knowledge of the water content (and other volatiles) of a magma is essential to understanding explosive volcanism. All of these could be found by experimental means, but such experiments have the disadvantage of being difficult to calibrate and very expensive, while giving exactly the same results as thermodynamic calculations. (Barton & Wyers 1991)

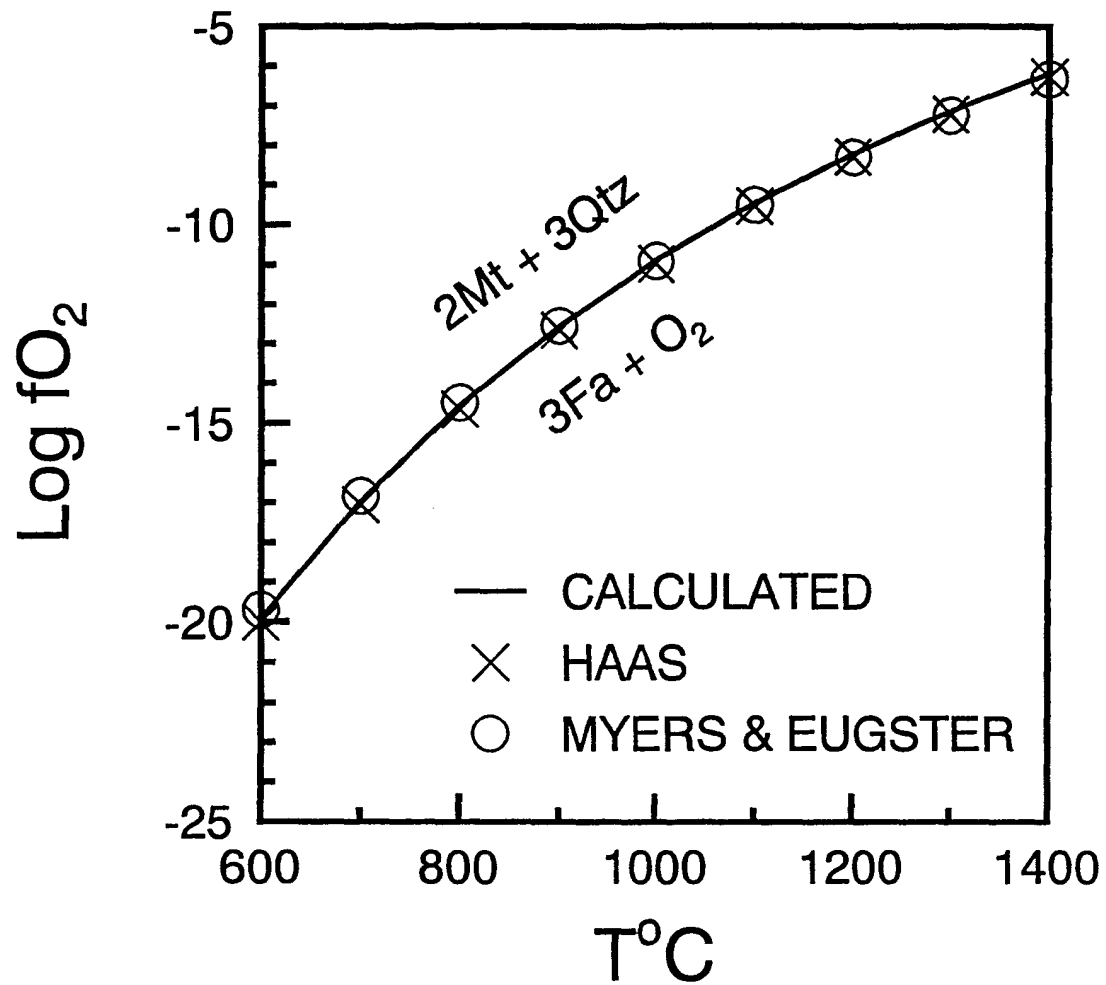
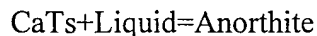
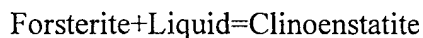


Figure 1

Methods

Compositions of igneous minerals were determined using a Cameca SX-50 electron microprobe with four wavelength-dispersive and one energy-dispersive spectrometers. The electron beam was set at 1 micron at 15kV. The current was set at 20na. Analyses were on several basalts from Santorini, Greece. In each, the rims and cores of plagioclase, pyroxene, olivine, and magnetite phenocrysts, as well as the groundmass, were analyzed. Analyses that represented the most primitive compositions were chosen for the calculations. For example, the feldspar analysis with the highest anorthite content and the olivine with the highest magnesium content were used.

A series of computer programs were written that give an estimation of the conditions of crystallization for a basaltic rock. The programs use the three following equilibria to find the pressure, temperature, and water content:



The majority of the programming went into determining the activities of each relevant phase. The first step is to calculate each phase's chemical potential, which is defined by

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

where R is the gas constant and a is the activity. The standard state chemical potential of the solid phases is calculated from

$$\mu^{\circ} = \Delta_f H^{T_r, P_r} + \int_{T_r}^T C_p dT - T [S^{T_r, P_r} + \int_{T_r}^T \frac{C_p}{T} dT] + \int_{P_r}^P V dP$$

where the first and third terms represent the standard state enthalpy of formation and the third law entropy at the reference temperature (298.15 K) and pressure (1 bar), and C and V represent the heat capacity and volume functions. (Berman & Brown 1987)

Since the silica in this system is in the form of a melt, it is necessary to define a standard state enthalpy and entropy for a pure liquid component. The enthalpy is found by the following equation:

$$H_{liq}^{\circ}(T_r) = \Delta_f H_{sol}^{\circ}(298) + \int_{298}^{T_{fus}} C_{p_{sol}}^{\circ} dT + \Delta H_{fus}^{\circ}(T_{fus}) + \int_{T_{fus}}^T C_{p_{liq}}^{\circ} dT$$

where the last two terms are the heat of fusion and the liquid heat capacity functions. The standard state entropy of a liquid component can be calculated by using the following equation:

$$S_{liq}^{\circ}(T_r) = S_{thirdlaw}^{\circ}(298) + \int_{298}^{T_{fus}} (C_{p_{sol}}^{\circ}/T) dT + \Delta S_{fus}^{\circ}(T_{fus}) + \int_{T_{fus}}^T (C_{p_{liq}}^{\circ}/T) dT$$

which is quite similar to the equation for enthalpy. (Lange & Carmichael 1990)

The chemical potentials for each phase are then used in

$$G = \sum_i^{nCS} x_i \mu_i$$

where G is the Gibbs free energy, ncs is the number of components, and x is the mole fraction. The activity is defined as the product of the mole fraction, x, and an activity coefficient, gamma. Using this definition, the previous equation can be expanded:

$$G_{solution} = \sum_i^{nCS} x_i [\mu_i^\circ + RT \ln x_i + RT \ln \gamma_i]$$

The first two terms define the ideal contribution to the Gibbs free energy of a solution, and the last term gives the nonideal contribution. This last term is called the excess Gibbs free energy and is written as

$$G_{excess} = \sum_{i=1}^{nCS} x_i RT \ln \gamma_i$$

(Berman & Brown 1988)

Finally, the excess Gibbs free energies are put into a series of equations determined experimentally by Davidson & Lindsley (1989), which are of the form

$$G_{excess} = \sum_i \sum_{j, j \neq i} W_{ij} X_i X_j (X_j + \sum_{k, k \neq i, j} X_k / 2) + \sum_i \sum_{j, j \neq i, k, k \neq i, j} W_{ijk} X_i X_j X_k$$

where W is a Margules-type term to describe non-ideal mixing and X is the mole fraction of the component. This model gives the distributions of cations over the M1 and M2 sites, and, at last, the activities.

Example

Probe analyses from sample SI-33 of pyroxene, plagioclase, olivine, and clinopyroxene were used in this calculation. (Table 1) The program calculates silica activities over a range of pressures and temperatures. These were then plotted on graphs for each reaction. (Fig. 2-4)

Figure 2

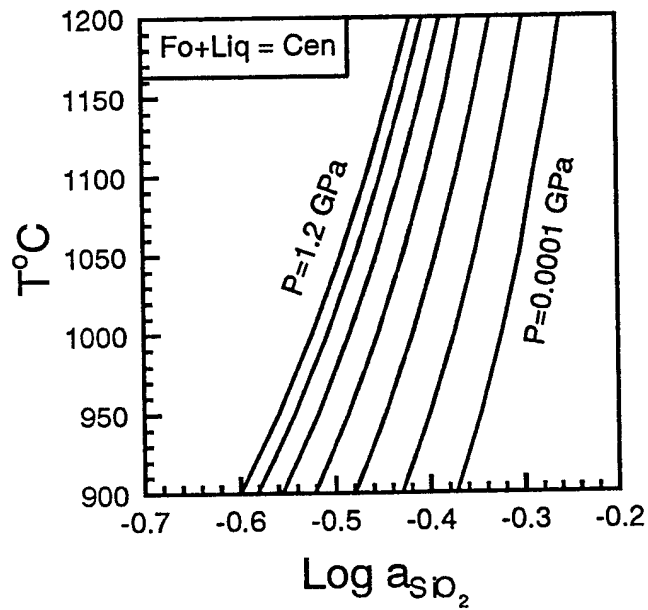


Figure 3

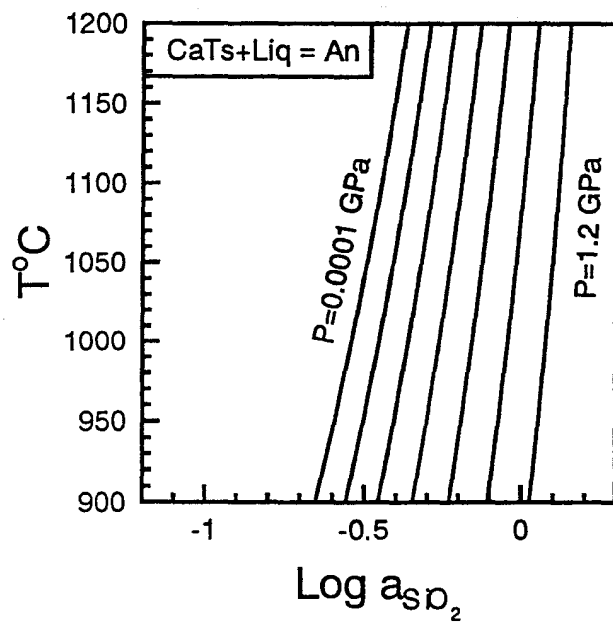
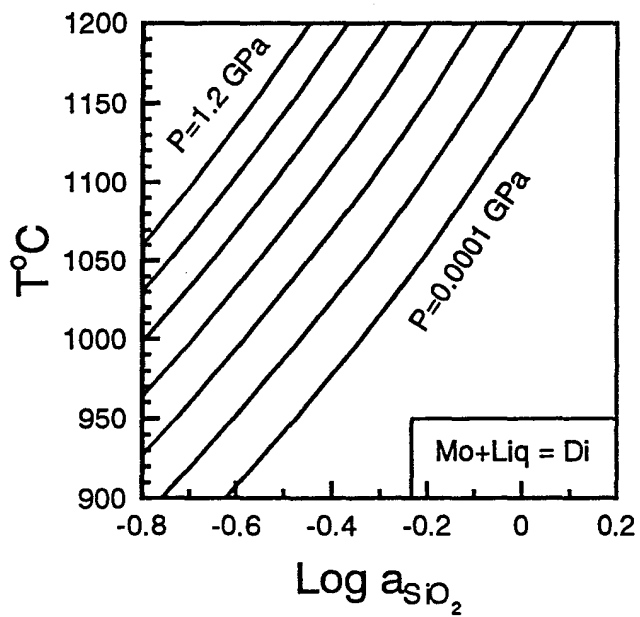


Figure 4



To arrive at a solution, the graphs were combined. Figures 2 and 4 produce the line of intersection shown in Figure 5, and the intersection of the graphs in Figures 3 and 4 is shown in Figure 6.

Figure 5

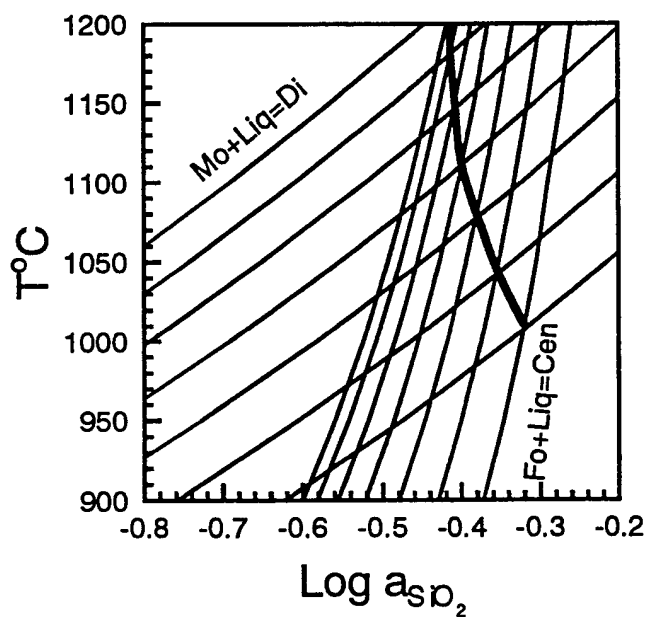
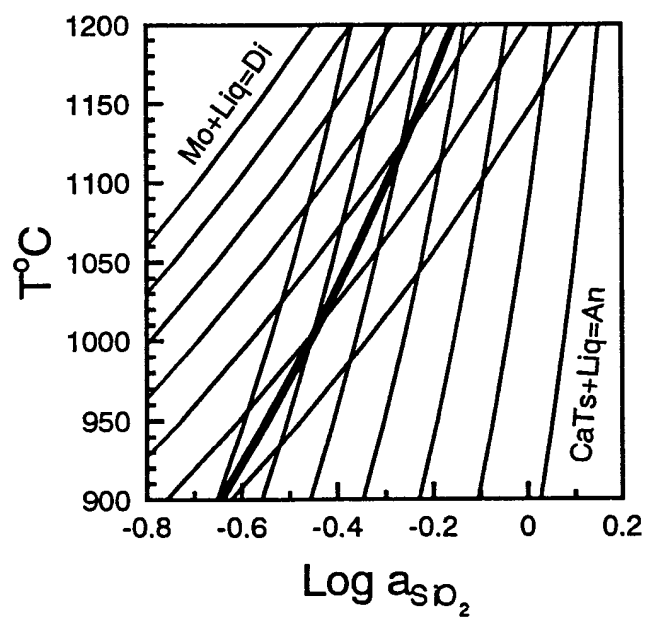
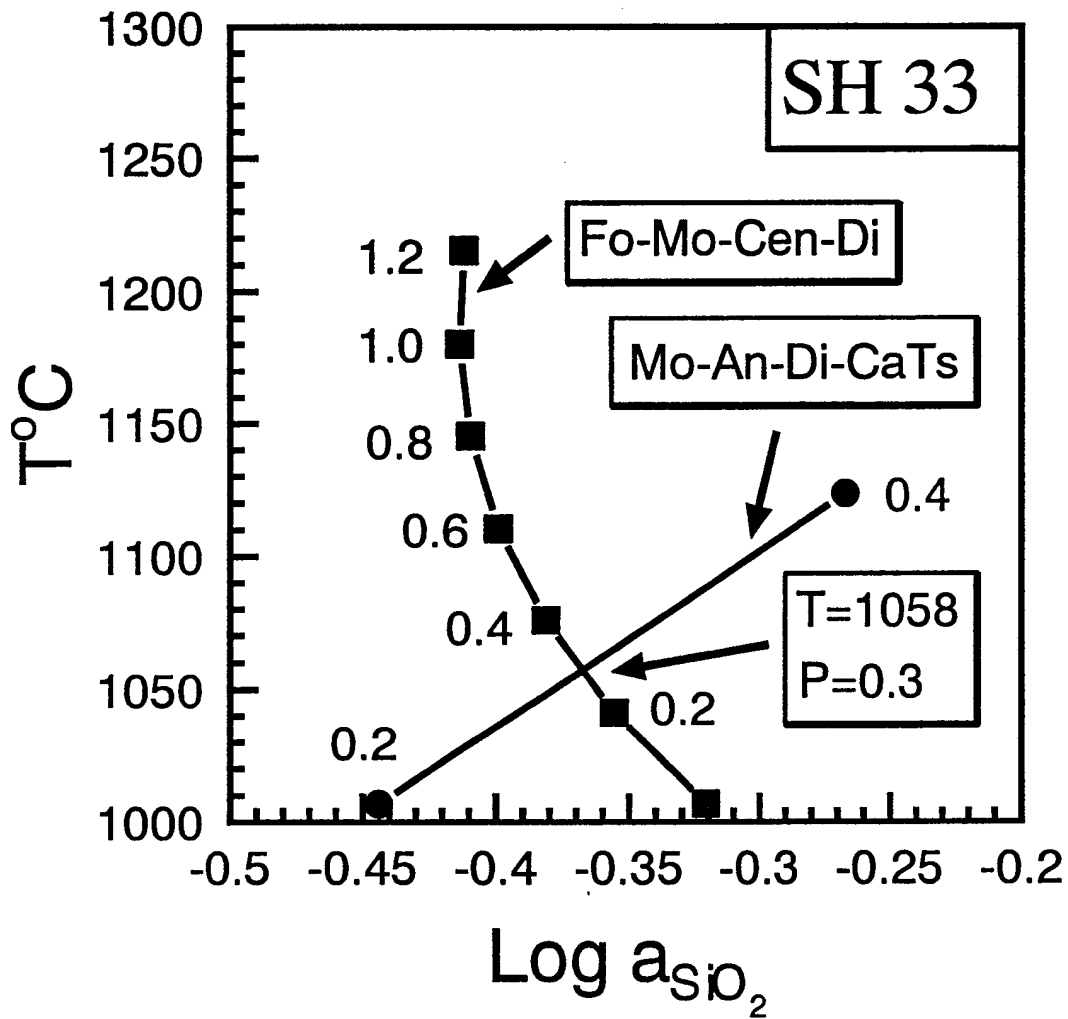


Figure 6



In Figure 7, the two previous results are combined and show that this basalt was formed at 1058 C and 0.3 GPa.

Figure 7



Conclusion

These results are confirmed by another, more recent model that involves water content in addition to temperature and pressure. Figure 8 shows the results, $T=1063.4$ C and $P=0.32$ GPa, which are extremely close to the first solution. Figures 9 & 10 give graphical solutions for the water content, first plotted against temperature ($H_2O=4.9\%$) and then against pressure ($H_2O=5.1\%$). (Sisson & Grove 1993) That all these results are, within error, consistent demonstrates the usefulness of thermodynamics in igneous petrology. As more data becomes available, more accurate results will be possible.

Figure 8

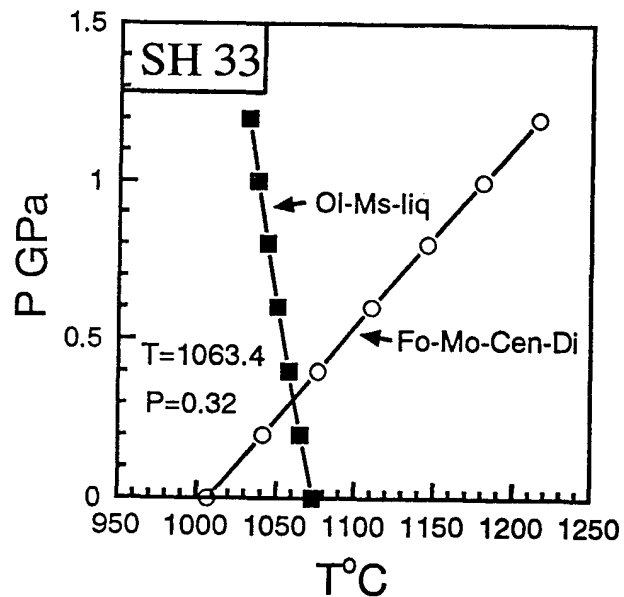


Figure 9

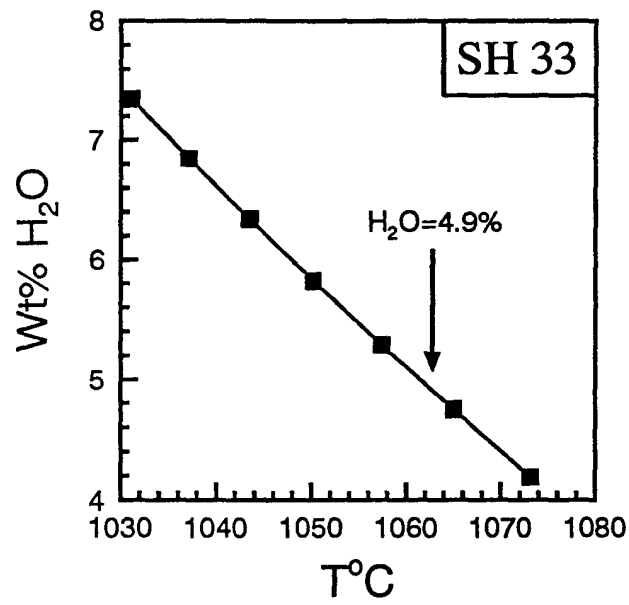


Figure 10

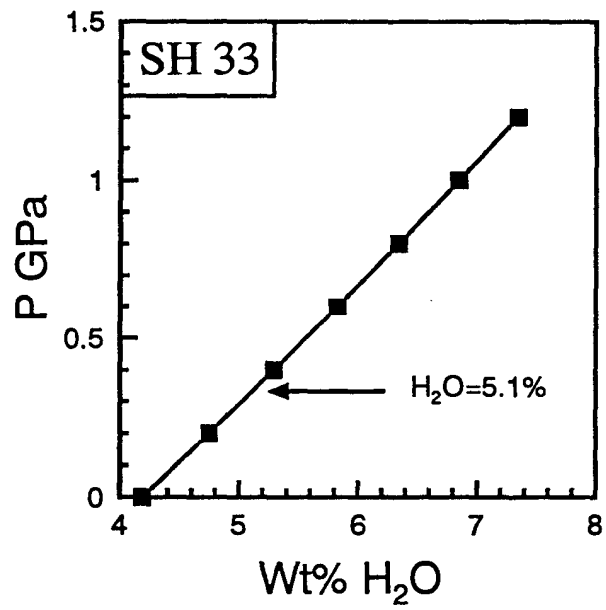


Table 1

DATA FOR SAMPLE SI 33

PYROXENE		WITH CALCULATED FE3+				PLAGIOCLASE			
SI02	51.15	SI	1.900	SI	1.894	SI02	46.69	SI	2.174
AL203	2.98	AL	0.130	AL	0.130	AL203	33.23	AL	1.823
TIO2	0.52	TI	0.015	TI	0.014	FEO	0.50	FE	0.020
CR203	0.43	CR	0.013	CR	0.013	MGO	0.08	MG	0.006
FE203	0.00	FE3+	0.000	FE3+	0.050	CAO	16.34	CA	0.815
FEO	7.08	FE2+	0.220	FE2+	0.169	NA2O	1.69	NA	0.152
MNO	0.24	MN	0.008	MN	0.008	K2O	0.06	K	0.003
MGO	16.59	MG	0.919	MG	0.915	BAO	0.00	BA	0.000
CAO	20.13	CA	0.801	CA	0.798	SUM	98.58	SUM	4.993
NA2O	0.25	NA	0.009	NA	0.009				
SUM	99.37	SUM	4.014	SUM	4.000				
		MGNO	- 0.807	MGNO	- 0.844				
		EN	= 0.474	EN	= 0.486			AN	= 0.840
		FS	= 0.113	FS	= 0.090			AB	= 0.157
		WO	= 0.413	WO	= 0.424			DR	= 0.003
								CS	= 0

SAMPLE/RUN : SI 33

DATA AS INPUT (NORMALIZED TO 100%) :

OLIVINE				CLINOPYROXENE			
SI02	40.57	SI	1.008	SI02	51.35	SI	1.889
AL203	0.00	AL	0.000	AL203	2.99	AL	0.130
TIO2	0.00	TI	0.000	TIO2	0.52	TI	0.014
FEO	12.94	FE	0.269	CR203	0.43	CR	0.013
MNO	0.22	MN	0.005	FE203	2.46	FE3+	0.088
MGO	46.10	MG	1.707	FEO	4.89	FE2+	0.150
NIO	0.00	NI	0.000	MNO	0.24	MN	0.007
CAO	0.17	CA	0.005	MGO	16.66	MG	0.914
TOTAL	100.00	SUM	2.992	CAO	20.21	CA	0.796
				NA2O	0.25	NA	0.018
				TOTAL	100.00	SUM	4.000
		FO	= 0.864			WO	= 0.4281
						EN	= 0.4911
						FS	= 0.0809

Acknowledgements

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