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Clinopyroxene solid solutions and water in magmas: results in the system phonolitic tephrite-H_2O

D. DOLFI AND R. TRIGILA

Istituto di Mineralogia e Petrografia, Università di Roma, Rome, Italy

ABSTRACT. Clinopyroxene solid solutions crystallized at $P_{tot} = 2$ kbar in the natural system phonolitic tephrite-H_2O (lava type from Etna eruption 1971) indicate a linear increase of $\ln X^{cpx}_{cats}$ with H_2O^{liq} %. After coupling this with the $\ln X^{cpx}_{cats}$ pressure dependence found through experiments, a simple relation has been set up for clinopyroxene- and plagioclase-bearing magmas. This relation allows us to calculate the amount of water dissolved in the melt, at any known pressure in the crustal range.

EXPERIMENTAL investigations on clinopyroxene solid solutions crystallized from lavas of the 1944 Vesuvius eruption and from leucite-bearing lavas of central Italy (Dolfi and Trigila, 1978*a* and *b*) have shown that the clinopyroxene compositional variations for a single rock can be related to the water content of the corresponding magmatic melt and that the influence of water on the pyroxene composition outweighs the effects of all the other physical variables, at least in the limited range of the investigated systems.

To obtain additional informations on the link between systems, compositions and clinopyroxene solid solutions, other experiments have been performed using a phonolitic tephrite (according to the nomenclature used by Romano *et al.*, 1979) lava sample from the Etna eruption 1971. In Table I the chemical analysis and the CIPW norm of the sample are reported. The eruptive event has been described in detail by Rittmann *et al.* (1971); the mineralogy and petrology of the lava flows and pyroclasts are described by Tanguy (1973) and Cagnetti *et al.* (1973); and experimental petrology data are given by Downes (1973) and Sato and Moore (1973).

Phase relations and composition of synthetic clinopyroxenes. The lava sample, finely powdered was used as starting material for the experiments. These have been carried out in the range 970 °C to 1200 °C at $P_{tot} = 2$ kbar using an internally heated pressure vessel (fig. 1). Runs lasted 48 h and have been buffered (f_{O_2} = NNO) letting hydrogen into the argon line at $P_{H_2} = 180$ psi. Temperatures are accurate to ± 4 °C of the nominal value. Iron loss by diffusion into the Pt-capsule walls has been estimated by wet-chemical analysis (Graham and Saunders, 1978) of two run products to be about 10 % of the initial amount. The same result has been obtained by mass-balance calculations using microprobe analyses of all phases present after runs. It is believed therefore that phase relations are not affected by the iron loss effect and even if the system has a different composition after runs, it can be considered approximately constant through the set of experiments, the compositions of crystallizing clinopyroxenes being biased in the same way. Water was added to the charges in variable amounts but never exceeding the saturation level in the liquid. The percentage of water dissolved in it was calculated from the amounts of glass in each charge obtained after experiments. The amounts of

TABLE I. *VC10 lava sample from Etna eruption 1971. Chemical analysis and C.I.P.W. norm*

SiO_2	47.5	mt	5.79
TiO_2	1.73	ap	1.24
Al_2O_3	17.0	il	3.34
Fe_2O_3	3.96	or	10.02
FeO	6.87	ab	20.03
MnO	0.19	an	24.48
MgO	5.85	wo	10.34
CaO	10.60	en	6.63
Na_2O	3.81	fs	3.04
K_2O	1.74	fo	5.56
P_2O_5	0.53	fa	2.96
SrO	0.13	ne	6.48
BaO	0.08		
L.O.I	0.07		
Total	100.06		

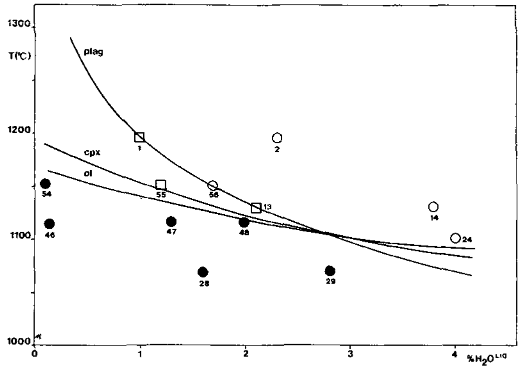


FIG. 1. Phase relations for the phonolitic tephrite lava sample VC10 at P_{tot} = 2 kbar. % H_2O^{liq} gives the wt. % of water dissolved in the liquid phase. Symbols—open circles: all liquid; open squares: plag + liq; dots: plag + ol + cpx + liq. Numbers refer to individual charges run in the system.

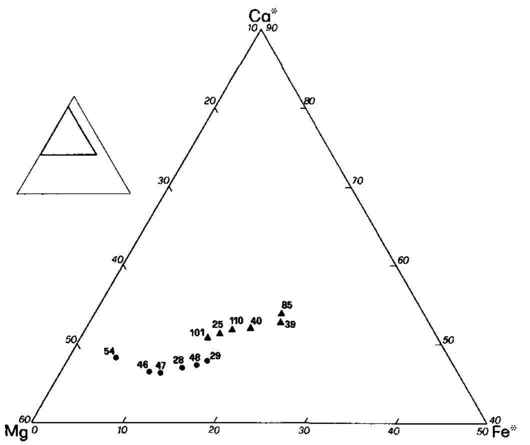
glass were estimated through mass-balance calculations carried out on the compositions of the phases present and checked by modal analysis of the charges. Considering the analytical errors of typical probe analyses on clinopyroxenes, the estimate of glass content in each run is believed to be accurate within 5% of its amount.

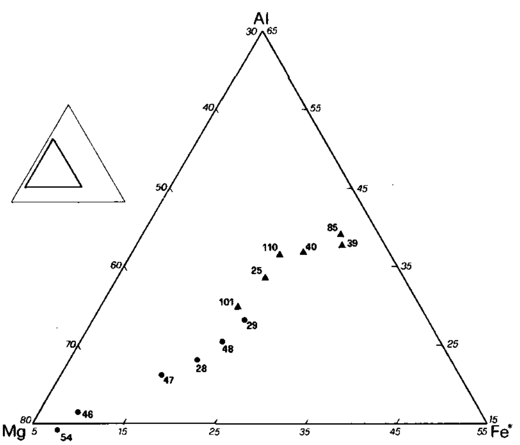
The data from the experiments show that plagioclase is the liquidus phase in the range: 0.1–2.7% H_2O^{liq}. This system behaves very differently from the tephritic leucitite system previously investigated (Dolfi and Trigila, 1978*a*); in that system plagioclase is the liquidus phase only if the melt is practically anhydrous, soon being replaced by leucite which is stable on the liquidus up to 2.0% H_2O^{liq}. From the above value to the H_2O saturation level, clinopyroxene appears on the liquidus.

Table II gives microprobe analyses of the clinopyroxenes crystallized at 2 kbar, and cations on the basis of six oxygens are also reported. As observed previously for Vesuvius clinopyroxenes, the water content in the melt correlates positively with Al^{IV} and Fe_{tot}; again a negative correlation with Si and Mg is shown. Ca and Al^{IV} do not vary significantly with water; Ti apparently correlates both with water in the melt, and with temperature. The

TABLE II. *Microprobe analyses of clinopyroxenes from experiments at P = 2 kbar*

no.	54	46	47	28	48	29
T °C	1152	1115	1115	1070	1115	1070
% H_2O^{liq}	0.1	0.3	1.2	1.6	2.3	2.8
phases	cpx-ol-plag-L	cpx-ol-plag-L	cpx-ol-plag-L	cpx-ol-plag-L	cpx-ol-plag-L	cpx-ol-plag-L
SiO_2	51.89	51.00	48.14	46.60	45.32	43.91
TiO_2	1.04	1.09	1.94	1.88	1.98	2.39
Al_2O_3	4.02	4.33	6.42	7.09	7.94	9.30
FeO	3.81	5.77	6.66	8.04	8.76	9.55
MnO	0.21	0.21	0.25	0.22	0.22	0.24
MgO	15.86	15.30	15.16	14.05	13.28	13.01
CaO	22.61	21.50	21.01	20.56	21.53	20.66
Na_2O	0.41	0.54	1.02	1.37	0.71	1.53
	99.85	99.52	100.60	99.81	99.74	100.59
Si	1.8976	1.8813	1.7784	1.7501	1.7133	1.6565
Ti	0.0286	0.0302	0.0539	0.0531	0.0563	0.0678
Al^{IV}	0.1024	0.1187	0.2216	0.2499	0.2867	0.3435
Al^{VI}	0.0708	0.0695	0.0579	0.0639	0.0670	0.0700
Fe^{2+}	0.1165	0.1780	0.2057	0.2525	0.2769	0.3012
Mn	0.0065	0.0066	0.0078	0.0070	0.0070	0.0077
Mg	0.8644	0.8412	0.8347	0.7864	0.7483	0.7315
Ca	0.8858	0.8496	0.8315	0.8272	0.8720	0.8350
Na	0.0291	0.0386	0.0731	0.0997	0.0520	0.1119
	4.0017	4.0137	4.0645	4.0898	4.0796	4.1250
X_{CATS}	0.0122	0.0130	0.0178	0.0212	0.0265	0.0295
$X_{CaMgSi_2O_6}$	0.6880	0.6237	0.5150	0.4562	0.4429	0.3712





FIGS. 2 and 3. FIG. 2 (*left*). $Ca(Ca + Na + K)$-Mg-$Fe(Fe_{tot} + Mn)$ diagram for clinopyroxenes crystallized experimentally. Dots represent the clinopyroxene compositions crystallized from the phonolitic tephrite lava sample VC10 (Etna 1971); analytical data and associated water contents in the liquid phase are reported in Table II. Triangles represent the clinopyroxene compositions obtained for the tephritic leucitite lava sample V1 (Vesuvius 1944). Data from Dolfi and Trigila (1978*b*). FIG. 3 (*right*). Al-Mg-Fe diagram for clinopyroxenes crystallized experimentally. Symbols and numbers same as for fig. 2.

increasing Fe_{tot} value, with increasing water, is probably due to the progressive addition of Fe^{3+} as shown roughly from the cation sum.

In fig. 2 the compositions of synthetic clinopyroxenes crystallized from the phonolitic tephrite lava sample VC10 (Etna 1971) and tephritic leucitite lava sample V1 (Vesuvius 1944) are projected on to the Ca*-Mg-Fe* triangle. The respective trends reflect a different chemical control for the two systems. This is explained by the buffering action of different co-precipitated phases: plag + cpx + ol in the Etna lava sample; plag + cpx + lc (101), or cpx + lc (25, 110, 40), or cpx + lc + mica (39, 85) in the Vesuvius lava sample (Dolfi and Trigila, 1978*b*).

In fig. 3 both sets of clinopyroxene compositions have been projected on to the Al-Mg-Fe* triangle, and they show a continued enrichment of Al with water. Trends observed in figs. 2 and 3, together with cation abundances in Table II, give a comprehensive picture of variations in pyroxene chemistry caused by the H_2O level in the melt. In particular the direct correlation of Al^{IV}, Fe^{3+} and the inverse correlation of Si with water content, highlight the usefulness of CATS and Fe-CATS components for estimating the water content in magmas.

In fig. 4 $\ln X^{cpx}_{cats}$-% H_2O^{liq} plot is shown. X^{cpx}_{cats} represents the thermodynamic molar fraction, calculated as follows: $X^{cpx}_{cats} = 4(X_{Ca})_{M2}(X_{Al})_{M1}(X_{Al} \cdot X_{Si})_T$; % H_2O^{liq} gives the estimated value of water percentage dissolved in the melt at the experimental conditions. Results reported in fig. 4 evidence linear trends between $\ln X^{cpx}_{cats}$ and % H_2O^{liq} despite the variability in the experimental temperatures. The temperature control appears instead if using the thermodynamic molar fraction of a major component of the clinopyroxene s.s., as for example, $CaMgSi_2O_6$ (fig. 5).

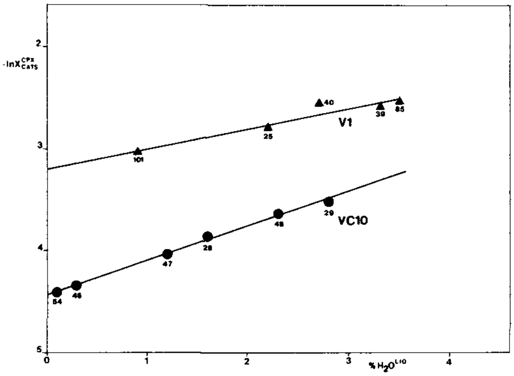


FIG. 4. Correlation between $\ln X^{cpx}_{cats}$ and wt. % H_2O^{liq} for clinopyroxenes crystallized experimentally at 2 kbar. VC10 phonolitic tephrite lava sample (Etna 1971). V1 tephritic leucitite lava sample (Vesuvius 1944).

A measure of the pressure dependence of $\ln X^{cpx}_{cats}$ can be obtained, expressing in terms of $\ln X^{cpx}_{cats}$ the compositions of the clinopyroxenes crystallized experimentally by Thompson (1974) from SK971 and EU13 lavas, similar in composition to the lavas from Etna and Vesuvius. His experiments, carried out above 8 kbar in the subliquidus region and under dry conditions, have been compared with others we made at 2 kbar (EU13 and VC10) and at atmospheric pressure (VC10). The slopes of regression lines from Thompson's results fit well with the results from our experiments, justifying the extrapolation at atmospheric pressure of the observed trends (fig. 6).

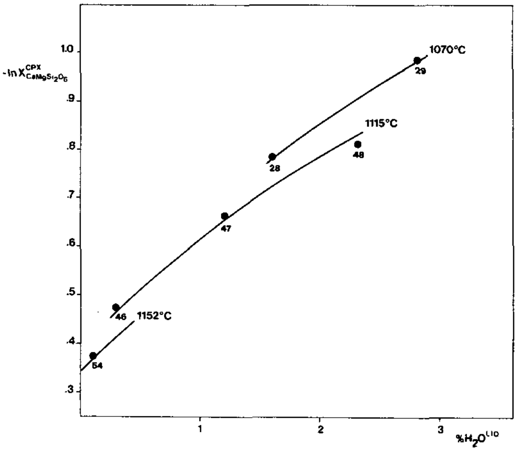


FIG. 5. Correlation between $\ln X^{cpx}_{CaMgSi_2O_6}$ and wt. % H_2O^{liq} for clinopyroxenes crystallized experimentally from sample VC10. The correlation is better understood if a temperature control on $X^{cpx}_{CaMgSi_2O_6}$ is considered. $X^{cpx}_{CaMgSi_2O_6} = (X_{Ca})_{M2}(X_{Mg})_{M1}(X_{Si})^2_T$.

Comparing results shown in figs. 4 and 6 we note there is a different response of clinopyroxene composition to the melt hydratation processes (as indicated by different slopes for the V1 and VC10 lava samples); on the contrary the effect of pressure on the clinopyroxene composition is the same for the reported systems; finally results on both fig. 4 and fig. 6 are not indicative of an effective control of temperature on thermodynamic X^{cpx}_{cats} at least for the range of experimental values.

Considering the above results it is possible to have an estimate of the water content in a melt from the composition of clinopyroxene, i.e. for Etna phonolitic tephrite this can be obtained according to the following expression:

$$\ln(X^{cpx}_{cats})_{P,T,H_2O^{liq}} = \ln(X^{cpx}_{cats})_{P^\circ,T^\circ,H_2O^{\circ liq}} + 0.338\,\%\,H_2O^{liq} + 0.572\cdot 10^{-4}(P-P^\circ)$$

where $\ln(X^{cpx}_{cats})_{P^\circ,T^\circ,H_2O^{\circ liq}}$ refers to a pyroxene at atmospheric pressure, in dry conditions and at whatever temperature in the magmatic range.

Concluding remarks. Obviously the reported relation only holds for lavas similar in composition to the investigated one, so many other experiments will be necessary if we want to express this relation in a more general form. There is an important influence of the liquid system composition on the gradient $\delta X^{cpx}_{cats}/\delta\,\%\ H_2O^{liq}$, probably due to different depolymerization rates of the liquid itself. Also we expect the gradient $\delta X^{cpx}_{cats}/\delta P$ will change if the liquid crystallizes clinopyroxenes with a crystal chemistry markedly different from the one we have found in the experiments: i.e. if $(X_{Ca})_{M2} < 0.8$.

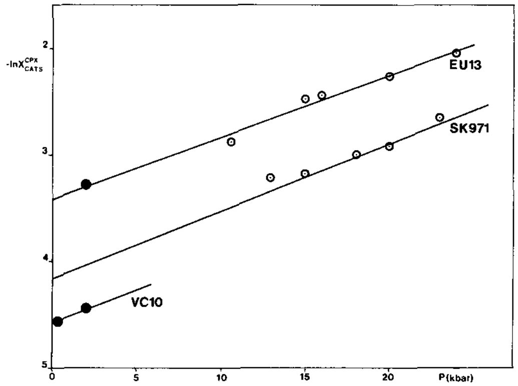


FIG. 6. Correlation between $\ln X^{cpx}_{cats}$ and P_{tot} under dry conditions. Circles: results by Thompson (1974) obtained on samples EU13 (leucitite) and SK971 (transitional basalt); dots: our results obtained on samples EU13 (leucitite) and VC10 (phonolitic tephrite).

However, considering the general occurrence of clinopyroxenes in lavas, we presume this is a rather promising and simple way to estimate the water content of a magma in equilibrium with some crystalline phases. This empyrical approach still gives better results than the one based on the evaluation of a^{cpx}_{cats} through thermodynamical calculations. In fact, as we deal with a multicomponent solid solution, the lack of thermochemical data which involve the Fe-CATS component inhibits a correct formulation of γ^{cpx}_{cats} which is changing according to variations of P,T, and X^{cpx}_{cats}.

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