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**Predicting Primary Crystalline Phase
and Liquidus Temperature Above or
Below 1050°C as Functions of
Glass Composition**

P.E. Redgate
G.F. Piepel

February 1996

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
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MASTER

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SUMMARY

This report presents the results of applying statistical empirical modeling techniques to predict: (i) primary crystalline phase at the liquidus temperature (T_L) and (ii) whether liquidus temperature is above or below 1050°C (100°C below a melting temperature of 1150°C).

Data used in modeling primary crystalline phase and liquidus temperature are from the Composition Variability Study (CVS) of Hanford waste glass compositions and properties. The majority of the 123 CVS glasses are categorized into one of 13 primary crystalline phases (at the liquidus temperature). They are also classified as to having T_L Above or Below 1050°C. Two common statistical methods used to model such categorical data are the multinomial logit and classification tree models.

The classification tree models provided an overall better modeling approach than did the multinomial logit models. The performance of models in this report should be compared to the performance of the revised "Development of Models and Software for Liquidus Temperature of Glasses of HWVP Products" models from Ecole Polytechnique. If the Ecole Polytechnique models perform better than the models discussed in this report, no additional effort on these models would be needed. However, if the converse is true, it may be worthwhile to invest additional effort on statistical empirical modeling methods.

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1.0 INTRODUCTION

This report presents the results of applying statistical empirical modeling techniques to predict : (i) primary crystalline phase at the liquidus temperature (T_L) and (ii) whether liquidus temperature is above or below 1050°C (100°C below a melting temperature of 1150°C). This report satisfies milestone # C95.02.01Y of the FY95 work scope for the glass formulation cost account of the Pacific Northwest Laboratory Vitrification Technology Development Project (PVTD).

The data used in fitting the primary crystalline phase and liquidus temperature models are from the Composition Variability Study (CVS) of Hanford waste glass compositions and properties (Hrma, Piepel, et al. 1994). CVS was planned and conducted in two major parts (CVS-I and CVS-II) consisting of five experimental and data analysis phases. This report used primary crystalline phase and liquidus temperature data from CVS-I and CVS-II, Phases 1,2 and 3. All of the glasses from these phases were melted at temperature less than 1200°C.

The majority of the 123 glasses listed in the CVS report are categorized into one of 13 primary crystalline phases (at the liquidus temperatures) and are listed in Section 2 along with their corresponding liquidus temperatures. Two common statistical methods used to model such categorical data are multinomial logit and tree-based models. These two modeling techniques are presented in Section 3 and results of applying the techniques to the CVS data are presented in Section 4. The results are discussed and conclusions are given in Section 5.

2.0 DATA USED IN MODELING

From 1989 to 1994, 123 nonradioactive glasses were melted and properties measured in five statistically-designed experimental phases. Glass composition is represented by the 10 components: SiO_2 , B_2O_3 , Al_2O_3 , Fe_2O_3 , ZrO_2 , Na_2O , Li_2O , CaO , MgO and Others (all remaining components). The 10 component glass compositions, primary crystalline phases at liquidus temperature, and liquidus temperatures are listed in Table 1. The primary crystalline phases listed in Table 1 are for two cases-- when spinel is treated as a primary phase and when is it not.

The non-spinel primary crystalline phase abbreviations used in Table 1 are as follows:

<u>Abbreviation:</u>	<u>Crystalline Phase:</u>
zircon	Zirconium-containing
casi	Calcium Silicate
olivine	Olivine
si	Silicon Dioxide
ortho	Orthopyroxene
clino	Clinopyroxene
hematite	Hematite
nepheline	Nepheline
cr2o3	Cr_2O_3
lial	Lithium Alumina Silicate
lisi	Lithium Silicate

As can be seen in Table 1, some of these crystalline phases were primary at the liquidus temperature for only a small number of glasses.

Table 1. CVS Glass Data Used in Modeling

Glass	Mass Fraction Compositions										Non-Spinel Primary Phase ^(a)	Spinel as Primary Phase ^(b)	Maximum Liquidus Temperature (°C) ^(c)
	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	ZrO ₂	Others			
CVS1-1	.4801	.1142	.1003	.0376	.0275	.0363	.0568	.0636	.0429	.0407	zircon	yes	977
CVS1-2	.5500	.0500	.0500	.0700	.1000	.0000	.0200	.1500	.0000	.0100	casi	.	942
CVS1-3	.4200	.2000	.0500	.0700	.0000	.0800	.0200	.1400	.0100	.0100	olivine	.	942
CVS1-4	.5700	.2000	.0900	.0100	.0200	.0800	.0200	.0000	.0000	.0100	si	.	957
CVS1-5	.5700	.0500	.0700	.0700	.0000	.0000	.1500	.0800	.0000	.0100	ortho	yes	1035
CVS1-6	.4400	.2000	.0500	.0700	.0000	.0000	.0200	.0000	.1200	.1000	zircon	.	>1118
CVS1-7	.5700	.0500	.0964	.0100	.1000	.0000	.0336	.0000	.1300	.0100	zircon	.	>1118
CVS1-8	.5363	.0500	.0837	.0100	.0000	.0800	.1500	.0000	.0800	.0100	.	.	>1118
CVS1-9	.4200	.1962	.0538	.0100	.0000	.0800	.1400	.0000	.0000	.1000	.	yes	>1118
CVS1-10	.5700	.0851	.0949	.0100	.0000	.0000	.0200	.1200	.0000	.1000	.	yes	>1118
CVS1-11	.4200	.1549	.0751	.0100	.1000	.0000	.0200	.1400	.0000	.0800	casi	yes	1035
CVS1-12	.4200	.1764	.0736	.0700	.1000	.0000	.1500	.0000	.0000	.0100	ortho	.	828
CVS1-13	.5700	.2000	.1862	.0100	.0000	.0000	.0200	.0038	.0000	.0100	.	.	.
CVS1-14	.4200	.2000	.1862	.0100	.0000	.0000	.0200	.0238	.1300	.0100	.	.	.
CVS1-15	.5589	.0500	.1211	.0700	.0000	.0800	.0200	.0000	.0000	.1000	olivine	.	866
CVS1-16	.4327	.0500	.1873	.0100	.0000	.0800	.0858	.1442	.0000	.0100	.	.	>1118
CVS1-17	.4545	.0500	.1455	.0100	.1000	.0000	.1400	.0000	.0000	.1000	casi	yes	1000
CVS1-18	.4214	.0500	.1186	.0700	.0200	.0800	.0200	.0000	.1300	.0900	zircon	.	>1118
CVS1-19	.4801	.1142	.1003	.0376	.0275	.0363	.0568	.0636	.0429	.0407	zircon	yes	961
CVS1-20	.4801	.1142	.1003	.0376	.0275	.0363	.0568	.0636	.0429	.0407	zircon	yes	966
CVS1-21	.5700	.2000	.0900	.0100	.0200	.0800	.0200	.0000	.0000	.0100	si	.	957
CVS1-22	.5363	.0500	.0837	.0100	.0000	.0800	.1500	.0000	.0800	.0100	.	.	>1118
CVS1-23	.5153	.0956	.1052	.0375	.0289	.0084	.1179	.0456	.0063	.0393	clino	yes	980
CVS2-1	.5226	.0874	.0700	.0600	.0000	.0500	.0400	.0800	.0100	.0800	olivine	yes	1048

(a) Primary crystalline phase when spinel phase was not considered. Primary phase was phase with maximum T_L . Undetermined crystalline phase is indicated by a ".".

(b) Spinel as primary phase if T_L for spinel crystals > T_L for any other phase. Spinel not as primary phase is denoted by a ".".

(c) The maximum liquidus temperature of spinel or non-spinel crystals was used in modeling.

Table 1. CVS Glass Data Used in Modeling (cont)

Glass	Mass Fraction Compositions										Non-Spinel	Spinel as	Maximum
	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	ZrO ₂	Others	Primary Phase ^(a)	Primary Phase ^(b)	Liquidus Temperature (°C) ^(c)
CVS2-2	.5017	.0700	.0883	.0600	.0700	.0000	.0450	.1100	.0300	.0250	casi	.	839
CVS2-3	.4645	.1320	.0700	.0435	.0700	.0100	.0450	.1032	.0368	.0250	zircon	.	931
CVS2-4	.5600	.1095	.0700	.0536	.0700	.0000	.0400	.0619	.0100	.0250	casi	.	810
CVS2-5	.4751	.1590	.1010	.0200	.0348	.0000	.0400	.0800	.0100	.0800	casi	yes	993
CVS2-6	.5373	.0700	.0700	.0382	.0700	.0046	.1200	.0159	.0100	.0641	clino	yes	939
CVS2-7	.4814	.1700	.0700	.0591	.0094	.0000	.0400	.0953	.0100	.0648	clino	yes	934
CVS2-8	.5115	.0700	.0985	.0600	.0000	.0500	.1140	.0610	.0100	.0250	ortho	yes	>1118
CVS2-9	.5431	.0944	.0924	.0600	.0000	.0000	.0712	.0138	.1000	.0250	zircon	.	1018
CVS2-10	.4694	.1700	.1306	.0200	.0000	.0000	.0669	.1043	.0100	.0288	.	yes	.
CVS2-11	.4915	.0751	.0833	.0600	.0700	.0100	.0400	.0100	.0935	.0665	zircon	.	1035
CVS2-12	.4683	.1700	.0700	.0466	.0700	.0100	.0400	.0901	.0100	.0250	clino	.	840
CVS2-13	.4937	.0700	.1692	.0225	.0300	.0500	.0400	.0896	.0100	.0250	clino	.	909
CVS2-14	.4600	.1313	.0802	.0486	.0500	.0200	.0400	.0243	.1000	.0457	zircon	.	>1118
CVS2-15	.4729	.0700	.1700	.0214	.0601	.0000	.0400	.0756	.0100	.0800	.	yes	956
CVS2-16	.5353	.1053	.1125	.0375	.0083	.0084	.0719	.0231	.0385	.0592	clino	yes	906
CVS2-17	.4801	.1142	.1003	.0376	.0275	.0363	.0568	.0636	.0429	.0407	zircon	yes	971
CVS2-18	.5353	.1053	.1125	.0375	.0083	.0084	.0719	.0231	.0385	.0592	clino	yes	895
CVS2-19	.5328	.1048	.1129	.0373	.0082	.0084	.0733	.0235	.0392	.0596	zircon	yes	862
CVS2-20	.5700	.0500	.1031	.0669	.0000	.0000	.0600	.0100	.1300	.0100	zircon	.	1081
CVS2-21	.5700	.1314	.0500	.0700	.0000	.0800	.0200	.0686	.0000	.0100	ortho	.	904
CVS2-22	.5700	.0500	.0735	.0700	.0000	.0800	.0200	.0365	.0000	.1000	olivine	yes	994
CVS2-23	.5700	.0522	.2000	.0100	.0800	.0000	.0200	.0578	.0000	.0100	casi	.	873
CVS2-24	.4464	.2000	.0736	.0700	.0000	.0000	.0200	.0961	.0000	.0939	.	yes	800
CVS2-25	.5059	.0500	.0841	.0700	.0800	.0000	.1500	.0033	.0000	.0567	ortho	yes	899
CVS2-26	.4431	.2000	.0512	.0700	.0800	.0000	.0200	.0257	.1000	.0100	zircon	.	1049
CVS2-27	.5463	.0500	.2000	.0155	.0000	.0800	.0200	.0782	.0000	.0100	.	.	<642

(a) Primary crystalline phase when spinel phase was not considered. Primary phase was phase with maximum T_L . Undetermined crystalline phase is indicated by a ".".

(b) Spinel as primary phase if T_L for spinel crystals > T_L for any other phase. Spinel not as primary phase is denoted by a ".".

(c) The maximum liquidus temperature of spinel or non-spinel crystals was used in modeling.

Table 1. CVS Glass Data Used in Modeling (cont)

Glass	Mass Fraction Compositions										Non-Spinel Primary Phase ^(a)	Spinel as Primary Phase ^(b)	Maximum Liquidus Temperature (°C) ^(c)
	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	ZrO ₂	Others			
CVS2-28	.5619	.0500	.2000	.0126	.0000	.0000	.0200	.0555	.0000	.1000	.	.	<642
CVS2-29	.4391	.2000	.0675	.0100	.0800	.0000	.0200	.0000	.0834	.1000	zircon	.	1108
CVS2-30	.5190	.2000	.0832	.0100	.0000	.0000	.1320	.0458	.0000	.0100	hematite	yes	1090
CVS2-31	.5700	.1843	.0500	.0331	.0800	.0000	.0200	.0526	.0000	.0100	si	.	939
CVS2-32	.5445	.0500	.2000	.0428	.0000	.0000	.0200	.0027	.1300	.0100	zircon	.	1066
CVS2-33	.4200	.0544	.2000	.0364	.0000	.0800	.0200	.0892	.0000	.1000	olivine	yes	967
CVS2-34	.4200	.1743	.2000	.0369	.0000	.0000	.0200	.1388	.0000	.0100	nepheline	.	736
CVS2-35	.4200	.0500	.2000	.0428	.0800	.0000	.0632	.1340	.0000	.0100	nepheline	.	941
CVS2-36	.5421	.0500	.0891	.0700	.0800	.0000	.1500	.0088	.0000	.0100	ortho	.	877
CVS2-37	.5700	.0839	.1061	.0700	.0000	.0000	.0200	.1400	.0000	.0100	nepheline	.	803
CVS2-38	.5147	.1109	.1044	.0100	.0000	.0800	.1428	.0272	.0000	.0100	olivine	yes	>1115
CVS2-39	.4838	.0500	.1362	.0700	.0000	.0800	.0742	.0258	.0700	.0100	zircon	.	1048
CVS2-40	.5040	.0639	.1500	.0421	.0200	.0500	.0200	.1000	.0200	.0300	clino	.	862
CVS2-41	.5325	.0694	.0781	.0700	.0500	.0200	.0300	.1000	.0200	.0300	clino	.	887
CVS2-42	.5675	.0500	.0625	.0700	.0320	.0380	.1000	.0300	.0200	.0300	clino	yes	1093
CVS2-43	.5070	.1477	.0500	.0653	.0200	.0300	.0300	.0500	.0700	.0300	zircon	.	1090
CVS2-44	.5700	.1078	.0500	.0699	.0500	.0200	.0200	.0623	.0200	.0300	clino	.	884
CVS2-45	.5299	.1106	.0500	.0595	.0200	.0500	.0308	.0592	.0200	.0700	clino	yes	894
CVS2-46	.5264	.1259	.0577	.0700	.0200	.0200	.0200	.0746	.0200	.0654	clino	yes	1004
CVS2-47	.5294	.0500	.1277	.0429	.0500	.0200	.0200	.0400	.0500	.0700	clino	.	919
CVS2-48	.4700	.1442	.0968	.0390	.0500	.0200	.0200	.0854	.0200	.0546	clino	.	868
CVS2-49	.5073	.1357	.0957	.0413	.0200	.0200	.0515	.0785	.0200	.0300	clino	yes	957
CVS2-50	.4801	.1142	.1003	.0376	.0275	.0363	.0568	.0636	.0429	.0407	zircon	yes	1025
CVS2-51	.5328	.1048	.1129	.0373	.0082	.0084	.0733	.0235	.0392	.0596	zircon	yes	899
CVS2-52	.6000	.0817	.0450	.0788	.0008	.0009	.0720	.0233	.0385	.0590	ortho	yes	973
CVS2-53	.5226	.0874	.0700	.0600	.0000	.0500	.0400	.0800	.0100	.0800	.	.	.

(a) Primary crystalline phase when spinel phase was not considered. Primary phase was phase with maximum T_L . Undetermined crystalline phase is indicated by a ".".

(b) Spinel as primary phase if T_L for spinel crystals > T_L for any other phase. Spinel not as primary phase is denoted by a ".".

(c) The maximum liquidus temperature of spinel or non-spinel crystals was used in modeling.

Table 1. CVS Glass Data Used in Modeling (cont)

Glass	Mass Fraction Compositions										Non-Spinel Primary Phase ^(a)	Spinel as Primary Phase ^(b)	Maximum Liquidus Temperature (°C) ^(c)
	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	ZrO ₂	Others			
CVS2-54	.5328	.1048	.1129	.0373	.0082	.0084	.0733	.0235	.0392	.0596	.	.	.
CVS2-55	.5328	.1048	.1129	.0373	.0082	.0084	.0733	.0235	.0392	.0596	cr2o3	yes	>1118
CVS2-56	.5328	.1048	.1129	.0373	.0082	.0084	.0733	.0235	.0392	.0596	clino	yes	1117
CVS2-57	.5328	.1048	.1129	.0373	.0082	.0084	.0733	.0235	.0392	.0596	cr2o3	.	1036
CVS2-58	.3900	.2000	.0500	.0700	.0200	.0800	.0200	.1500	.0100	.0100	olivine	.	906
CVS2-59	.4380	.1718	.1268	.0727	.0375	.0005	.0200	.1150	.0075	.0102	si	.	715
CVS2-60	.5281	.0876	.1725	.0743	.0063	.0005	.0200	.0925	.0075	.0107	si	.	788
CVS2-61	.5281	.0664	.1200	.0730	.0000	.0000	.0200	.1625	.0175	.0125	si	.	792
CVS2-62	.5579	.1765	.1125	.0156	.0500	.0005	.0200	.0500	.0075	.0095	.	.	<554
CVS2-63	.3232	.1717	.1900	.0051	.1000	.0000	.0200	.1800	.0000	.0100	nepheline	.	927
CVS2-64	.5697	.0509	.0925	.0642	.0025	.0008	.0812	.0288	.0431	.0663	ortho	yes	983
CVS2-65	.5344	.1128	.0860	.0697	.0007	.0004	.0013	.0196	.1548	.0203	zircon	.	>1114
CVS2-66	.5175	.0917	.1211	.0523	.0097	.0061	.0388	.1180	.0026	.0422	nepheline	yes	>1114
CVS2-67	.4596	.1587	.1086	.0583	.0024	.0001	.0004	.2043	.0000	.0076	cr2o3	.	1022
CVS2-68	.5040	.1355	.0797	.0696	.0007	.0002	.0046	.1640	.0001	.0416	cr2o3	.	>1114
CVS2-69	.5660	.0781	.0664	.0713	.0079	.0032	.0334	.0816	.0005	.0916	cr2o3	yes	>1114
CVS2-70	.4854	.1418	.0812	.0691	.0008	.0008	.0080	.1819	.0005	.0305	cr2o3	.	>1114
CVS2-71	.5697	.0509	.0925	.0642	.0025	.0008	.0812	.0288	.0431	.0663	ortho	yes	1004
CVS2-72	.5175	.0917	.1211	.0523	.0097	.0061	.0388	.1180	.0026	.0422	nepheline	yes	794
CVS2-73	.5040	.1355	.0797	.0696	.0007	.0002	.0046	.1640	.0001	.0416	lial	.	816
CVS2-74	.5660	.0781	.0664	.0713	.0079	.0032	.0334	.0816	.0005	.0916	clino	yes	1066
CVS2-75	.4854	.1418	.0812	.0691	.0008	.0008	.0080	.1819	.0005	.0305	lial	.	815
CVS2-76	.5018	.0600	.1800	.0632	.0400	.0050	.1050	.0200	.0050	.0200	clino	.	761
CVS2-77	.4550	.0600	.1800	.0700	.0050	.0050	.0050	.0200	.1100	.0900	zircon	.	1027
CVS2-78	.5600	.1600	.0500	.0254	.0050	.0400	.0699	.0200	.0497	.0200	zircon	.	1129
CVS2-79	.5479	.1600	.0500	.0121	.0050	.0050	.1050	.0200	.0050	.0900	si	yes	>1154

(a) Primary crystalline phase when spinel phase was not considered. Primary phase was phase with maximum T_L . Undetermined crystalline phase is indicated by a ".".

(b) Spinel as primary phase if T_L for spinel crystals > T_L for any other phase. Spinel not as primary phase is denoted by a ".".

(c) The maximum liquidus temperature of spinel or non-spinel crystals was used in modeling.

Table 1. CVS Glass Data Used in Modeling (cont)

Glass	Mass Fraction Compositions										Non-Spinel Primary Phase ^(a)	Spinel as Primary Phase ^(b)	Maximum Liquidus Temperature (°C) ^(c)
	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	ZrO ₂	Others			
CVS2-80	.5074	.1600	.0500	.0176	.0050	.0400	.1050	.0200	.0750	.0200	zircon	.	>1154
CVS2-81	.4400	.0600	.1734	.0700	.0050	.0400	.1050	.0200	.0050	.0816	.	.	>1154
CVS2-82	.5600	.0950	.1800	.0700	.0050	.0400	.0050	.0200	.0050	.0200	lisi	.	745
CVS2-83	.4900	.0951	.1800	.0699	.0400	.0050	.0050	.0200	.0050	.0900	lisi	.	741
CVS2-84	.4550	.0600	.1800	.0700	.0050	.0050	.1050	.0200	.0800	.0200	zircon	.	966
CVS2-85	.4400	.0600	.1800	.0700	.0050	.0200	.0050	.1700	.0050	.0450	.	.	>1150
CVS2-86	.4764	.0600	.1800	.0136	.0400	.0050	.0050	.1700	.0050	.0450	nepheline	.	1015
CVS2-87	.4983	.0800	.1800	.0180	.0137	.0050	.0250	.0987	.0613	.0200	.	.	<571
CVS2-88	.4597	.0600	.1403	.0700	.0400	.0050	.0250	.1050	.0750	.0200	zircon	.	929
CVS2-89	.4400	.1171	.1800	.0100	.0400	.0050	.1050	.0200	.0629	.0200	clino	.	838
CVS2-90	.5600	.1600	.0542	.0700	.0050	.0050	.1008	.0200	.0050	.0200	ortho	.	897
CVS2-91	.5600	.1600	.1050	.0100	.0050	.0400	.0050	.0200	.0050	.0900	si	yes	886
CVS2-92	.4400	.1600	.1000	.0700	.0050	.0400	.0050	.0200	.0700	.0900	zircon	yes	905
CVS2-93	.4400	.1337	.1279	.0700	.0098	.0050	.0986	.0200	.0050	.0900	clino	yes	794
CVS2-94	.4400	.1600	.1800	.0526	.0400	.0050	.0271	.0703	.0050	.0200	casi	.	663
CVS2-95	.4895	.1112	.1671	.0428	.0113	.0166	.0897	.0367	.0041	.0310	clino	.	804
CVS2-96	.4801	.1142	.1003	.0376	.0275	.0363	.0568	.0636	.0429	.0407	zircon	yes	1010
CVS2-97	.5328	.1048	.1129	.0373	.0082	.0084	.0733	.0235	.0392	.0596	zircon	yes	887
CVS2-98	.4200	.1743	.2000	.0369	.0000	.0000	.0200	.1388	.0000	.0100	nepheline	.	740
CVS2-99	.5203	.0969	.0980	.0356	.0097	.0077	.1019	.0523	.0199	.0577	clino	yes	988
CVS2-100	.5329	.0740	.0626	.0596	.0035	.0012	.1229	.0286	.0443	.0704	ortho	yes	1030

(a) Primary crystalline phase when spinel phase was not considered. Primary phase was phase with maximum T_L . Undetermined crystalline phase is indicated by a ".".

(b) Spinel as primary phase if T_L for spinel crystals > T_L for any other phase. Spinel not as primary phase is denoted by a ".".

(c) The maximum liquidus temperature of spinel or non-spinel crystals was used in modeling.

3.0 MODELING CATEGORICAL DATA

In categorical data, the response variable (variable of interest) is not given on a continuous scale, but rather is classified into two or more categories. For the 123 CVS data points, the primary crystalline phase at the liquidus temperature was classified into one of 13 categories: Zirconium-containing, Calcium Silicate, Olivine, Silicon Dioxide, Orthopyroxene, Clinopyroxene, Hematite, Nepheline, Cr_2O_3 , Lithium Alumina Silicate and Lithium Silicate. Liquidus temperature was measured for most of the CVS glasses, but for some glasses it was only determined to be greater than a particular temperature (e.g., $>1118^\circ\text{C}$). Because of the mix of quantitative and semi-quantitative liquidus temperature data, and because modeling liquidus temperature directly as a function of glass composition is very difficult, it was decided to classify each CVS glass as having liquidus temperature "above" or "below" 1050°C . Models were then developed for predicting this binary categorical response variable.

Two common statistical modeling techniques for categorical data are multinomial logit and classification tree. The multinomial logit model predicts the probabilities of an observation belonging to the possible categories and is given by:

$$\text{Probability of category } j = p_j(x) = \begin{cases} \frac{e^{x \cdot \beta_j}}{(1 + \sum_{j=1}^{(g-1)} e^{x \cdot \beta_j})} , & j = 1, 2, \dots, g-1 \\ \frac{1}{(1 + \sum_{j=1}^{(g-1)} e^{x \cdot \beta_j})} , & j = g \end{cases}$$

for point x

such that $\sum_{j=1}^g p_j = 1$

where, g is the number of categories,
 x is the vector of predictor variables,
 β is the vector of coefficients.

In this application, the vector x of predictor variables consists of the mass fractions of the 10 oxide components of the glass (SiO_2 , B_2O_3 , Al_2O_3 , Fe_2O_3 , ZrO_2 , Na_2O , Li_2O , CaO , MgO and Others).

Classification tree models classify observations into categories by successively splitting a data set into increasingly homogeneous subsets of category memberships until it is infeasible to continue. Classification tree models are so-called because the primary method of displaying the model fit is in the form of a binary tree (see Figure 1 in Section 4).

A common statistic to determine how well the multinomial logit and classification tree models fit a data set is the mis-classification rate. The mis-classification rate is the percentage of time the models will incorrectly classify an observation into a category. For the logit models, an observation is classified into the category having the largest probability. For classification tree models, each data point is classified (predicted) into one of the possible categories. For both modeling approaches, "predicted" classifications are compared to the "actual" classifications of the data points, and the number of mis-classifications is determined. The mis-classification rate for both logit and classification tree models is computed by dividing the number of mis-classifications by the total number of classifications (i.e., the total number of data points). For convenience, mis-classification rates are multiplied by 100% and expressed as percentages.

Model validation is a technique to see how well a model will predict using independent data (i.e., data not used in fitting the model). Since the nature of this study was to assess the value of these modeling tools, model validation was not of great interest at this time.

4.0 MODEL FITTING RESULTS

The results of fitting the multinomial logit and classification tree models to predict the primary crystalline phase at liquidus temperatures, and whether T_L is above or below 1050°C are discussed in Sections 4.1 and 4.2, respectively.

4.1 Primary Crystalline Phase Model Fitting Results

In fitting a multinomial logit model to categorical data, it is ideal to have at least 20 observations in each category. As seen in Table 2, many categories contain a small number of observations. Hence, the first task before the multinomial logit model could be fit to the CVS primary crystalline phase data was to reduce the number of categories.

Table 2. Frequency of Spinel and Non-Spinel Primary Phases

<u>Phase</u>	<u>Non-Spinel Primary Phase # of Observations</u>	<u>Spinel as Primary Phase # of Observations</u>
Spinel	----	48
Clinopyroxene	23	9
Zirconium-containing	29	15
Calcium Silicate	8	5
Olivine	7	3
Silicon Dioxide	8	6
Orthopyroxene	11	4
Hematite	1	0
Nepheline	8	3
Na-Zr Silicate	3	3
Cr ₂ O ₃	6	4
Lithium Silicate	2	2
Lithium Alumina Silicate	2	2

A first attempt to reduce the number of categories was to classify the glasses into three primary (non-spinel) crystalline phases: Zirconium-containing, Clinopyroxene and "Remaining" (all other non-spinel phases). The logit model was then fit to these three categories using the 10 component glass compositions as predictor variables. This fit yielded a mis-classification rate of 35.6%. In an attempt to reduce the mis-classification rate, other

primary crystalline phase categories and model forms were tried. This included fitting the classification tree model to the CVS primary crystalline phase data as well. These different categories for the logit and tree models and their corresponding mis-classification rates are summarized in Table 3.

Table 3. Results of Categories and Model Forms Used to Predict Primary Crystalline Phase

Categories	Mis-Classification Rates	
	Logit Model	Classification Tree Model
Zirconium-containing, Clinopyroxene & Remaining (non-spinel)		
• 10 components	35.6%	10.9%
• 10 components + Fe_2O_3 x Others	32.9%	
• 10 components + Na_2O x Al_2O_3	31.7%	
Spinel, Not Spinel	6.7%	5.6%
Spinel, Clinopyroxene, Zirconium-containing	N/A *	14.1%
Spinel, Zirconium-containing & "Remaining" phases	N/A *	19.3%

* N/A = not enough data in a category for the logit model to estimate all the parameters.

The reasons for the choosing the categories in Table 3 were:

Zirconium-containing, Clinopyroxene and Remaining (non-spinel):

This grouping of primary crystalline phases was a first attempt to reduce the number of categories. As seen in Table 2, Clinopyroxene and Zirconium-containing phases had the largest number of observations, so grouping glasses into these two categories and "remaining" (non-spinel) phases provided a logical first selection.

Spinel, Not Spinel:

This particular grouping was used to tell if a glass, at higher temperatures, would form spinel crystals (which may cause melter problems).

Spinel, Clinopyroxene, and Zirconium-containing:

This grouping was chosen to correspond to the 3 first-order mixture models for T_L in the CVS report. If, given a glass composition, the model could predict when the glass would form Spinel, Clinopyroxene or Zirconium-containing crystals, then the corresponding first-order mixture model could be used to predict the liquidus temperature of the glass.

Spinel, Zirconium-containing and "Remaining":

These categories were chosen since there was some concern that Spinel and Zirconium-containing crystals might still exist and cause melter problems at higher temperatures.

It should be noted that some of the minor glass components (e.g., NiO, Cr_2O_3), which make up the "Others" composition, were used as predictor variables in the multinomial logit model to predict primary crystalline phase. This was unsuccessful since all but one of the CVS glasses used in this study have the same "Others" mix, and there was no variability among the minor components to estimate the corresponding coefficients.^(a)

Figure 1 gives the classification tree for predicting Zirconium-containing, Clinopyroxene and Remaining (non-spinel) primary crystalline phases. Figure 2 gives the classification tree for predicting Spinel and Non-Spinel primary crystalline phases. Figure 3 gives the classification tree for predicting Spinel, Clinopyroxene and Zirconium-containing primary crystalline phases. Figure 4 gives the classification tree for Spinel, Zirconium-containing and Remaining (non-spinel) primary crystalline phases. The primary phase predictions given in Figures 1 through 4 can be made by following the appropriate "branch" of the tree. For example, in Figure 1, if ZrO_2 is greater than 0.0334, then the tree splits to the right and a prediction of Zirconium-containing primary crystalline phase is made.

^(a) As discussed by Hrma, Piepel, et al.(1994), several "Others" mixes were studied in CVS. However, most of these did not have appropriate primary crystalline phase data allowing them to be used for modeling purposes.

Figure 1. Prediction of Zirconium Containing, Clinopyroxene and "Remaining" Crystalline Phases. Numbers next to vertical lines represent number of data points.

Figure 2. Prediction of Spinel, No Spinel Primary Crystalline Phase. Number next to vertical line represents number of data points.

Figure 3. Prediction of Zirconium-Containing, Spinel or Clinopyroxene Crystalline Phase. Number next to vertical line represents number of data points.

Figure 4. Prediction of Zirconium-Containing, Spinel, or "Remaining" Crystalline Phases. Number next to vertical line represents number of data points.

If, however, ZrO_2 is less than 0.0334, the tree splits to the left and then if ZrO_2 is less than 0.0003, a "Remaining" Crystalline Phase is predicted as the primary crystalline phase. If ZrO_2 is greater than 0.0003, the tree splits to the right and continues in this fashion until a terminal point is reached and a primary crystalline phase prediction is made.

Table 4 contains the model coefficients for the logit model prediction of Spinel, Not Spinel as the primary crystalline phase. The coefficients, when given a particular glass composition, will produce a probability of the glass being classified into Spinel (using Spinel estimates) or Not-Spinel (using Not-Spinel estimates). A correct classification is given to the category with the largest probability. The other logit model coefficients are not given because of their poor prediction performance.

Table 4. Logit Model Coefficients for Predicting Spinel, Not Spinel Primary Crystalline Phase

<u>Component</u>	<u>Component Estimate</u>	
	<u>Spinel</u>	<u>Not-Spinel</u>
SiO_2	-9.7153	9.7153
B_2O_3	-13.9926	13.9926
CaO	-49.4018	49.4018
Na_2O	-34.5037	34.5037
Li_2O	-49.9467	49.9467
MgO	3.1815	-3.1815
Al_2O_3	40.3763	-40.3763
ZrO_2	-30.7173	30.7173
Fe_2O_3	88.3049	-88.3049
Others	139.0	-139.0

4.2 Liquidus Temperature Model Fitting Results

The multinomial logit and classification tree models were both fit to the liquidus temperature data in Table 1, which was first classified as either "above" or "below" 1050°C . The multinomial logit model fitted to this binary categorical data set yielded a mis-

classification rate of 11.5%. Table 5 gives the model coefficients for this fit. The classification-tree model fitted to the "above" or "below" 1050°C data produced a mis-classification rate of 11.0%. Figure 5 shows the resulting classification tree of this fit.

Table 5. Logit Model Coefficients for Predicting "Above" or "Below" 1050°C T_L

<u>Component</u>	<u>Component Estimate</u>	
	<u>Above 1050°C</u>	<u>Below 1050°C</u>
SiO ₂	-.6041	.6041
B ₂ O ₃	-7.4664	7.4664
CaO	-31.0836	31.0836
Na ₂ O	-21.4266	21.4266
Li ₂ O	-52.2817	52.2817
MgO	19.6457	-19.6457
Al ₂ O ₃	17.3052	-17.3052
ZrO ₂	48.4889	-48.4889
Fe ₂ O ₃	21.6246	-21.6246
Others	16.6947	-16.6947

5.0 DISCUSSION AND CONCLUSIONS

Overall, for predicting the primary crystalline phase based on glass composition, the classification-tree modeling approach provided a better fit than did the multinomial logit models. The mis-classification rates for the "tree" models were lower than those of the logit models. The logit model did seem to predict well for spinel and non-spinel crystalline phase, (mis-classification rate of 6.7%), but this particular model does not yield any information about the other crystalline phases. If a glass is classified into "non-spinel" phase, there is no way to tell what that "non-spinel" phase is. The same can be said for the logit model prediction of Spinel and Not-Spinel primary crystalline phase.

The performance of models in this report should be compared to the performance of the revised "Development of Models and Software for Liquidus Temperature of Glasses of HWVP Products" models from Ecole Polytechnique. If the Ecole Polytechnique models

perform better than the models discussed in this report, no additional effort on these models would be needed. However, if the converse is true, it may be worthwhile to invest additional effort on statistical empirical modeling methods.

Figure 5. Prediction of Above or Below 1050°C T_L . Number next to vertical line represents number of data points.

6.0 QUALITY ASSURANCE

The work in this report was conducted in accordance with QA Impact Level II requirements as defined by PNL's quality assurance manual PNL-MA-70. Specific QA requirements applicable to this work are defined in the PNL Vitrification Technology Development (PVTD) project QA plan WTC-006.

7.0 REFERENCES

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