

The First Thousand Years
of Glass-Making in the
Ancient Near East:
Compositional Analyses of Late
Bronze and Iron Age Glasses

Wendy Reade

ARCHAEOPRESS ARCHAEOLOGY



ARCHAEOPRESS PUBLISHING LTD
Summertown Pavilion
18-24 Middle Way
Summertown
Oxford OX2 7LG
www.archaeopress.com

ISBN 978-1-78969-703-2
ISBN 978-1-78969-704-9 (e-Pdf)

© W Reade and Archaeopress 2021

All rights reserved. No part of this book may be reproduced, or transmitted, in any form or by any means, electronic, mechanical, photocopying or otherwise, without the prior written permission of the copyright owners.

This book is available direct from Archaeopress or from our website www.archaeopress.com

For my father
Peter C Reade
1930 - 2009

'... there is still merit in the simple notion that if you don't know what an object is made of, you don't really know much about it.'

Brill 1987: 1

Contents

Contents	i
Preface	xiii
Acknowledgements.....	xiv
Abbreviations	xvi
Chronology	xvi
Technical Terms	xvi
Oxides	xvi
Elements.....	xvi
Chapter 1	1
Introduction, Background and Aims	1
1.1 Introduction (Figure 1-1).....	1
1.2 Historical Background of Early Glass.....	2
1.3 The Early Glass Industry.....	4
1.4 Object Studies.....	7
1.5 Early Chemical Investigations	7
1.6 Silica.....	9
1.7 Lime	10
1.8 Plant Ash	11
1.9 Mineral Soda.....	12
1.10 Colourants, Opacifiers and Decolourants	13
1.10.1 Cobalt	14
1.10.2 Antimony as an Opacifier and a Decolourant	15
1.11 Trace Element Analyses	16
1.12 Analyses of LBA Near Eastern Glasses	17
1.13 Analyses of LBA Egyptian Glasses	17
1.14 Analyses of IA Glasses	19
1.15 Glass Raw Materials in Brief.....	19
1.16 Aims	19
Chapter 2	23
Methods for Compositional Analyses and Data Interpretation	23
2.1 Introduction	23
2.2 Sampling	23
2.3 Scanning Electron Microscopy and Electron Probe Microanalysis (SEM and EPMA).....	24
2.3.1 Introduction	24
2.3.2 Sample Preparation for SEM-EDS and EPMA	26
2.3.3 SEM-EDS Instrument and Analytical Protocol	27
2.3.3.1 Standards	27
2.3.3.2 Precision and Error	27
2.3.4 EPMA Instrument and Analytical Protocol	27
2.3.4.1 Primary Standards	27
2.4 Solution ICP-MS	29
2.4.1 Sample Preparation ICP-MS.....	29
2.4.2 ICP-MS Instrument and Analytical Protocol.....	29
2.5 Organisation and Presentation of Data	31
2.5.1 Introduction	31
2.5.2 Organisation of Trace Element Data.....	32
2.5.3 Rare Earth Elements (REE)	33
2.5.4 Presentation of Oxide and Elemental Data.....	34
2.5.5 Statistical Methods Used.....	34

Chapter 3	37
NUZI: Late Bronze Age Glasses Results of Compositional Analyses	37
3.1 Introduction to the Site	37
3.1.1 The Excavations	38
3.1.2 The Glass	39
3.1.3 Summary of Samples	40
3.2 Base Glass Composition	43
3.2.1 Summary.....	46
3.3 Trace Element Composition.....	46
3.3.1 Rare Earth Elements (REE)	46
3.3.2 Sediment-Related Elements (SRE)	49
3.3.3 Alkali and Alkaline Earth Elements	50
3.3.4 Colourants and Opacifiers.....	53
3.4 General Conclusions	56
Chapter 4	58
Pella: Late Bronze Age Glasses Results of Compositional Analyses	58
4.1 Introduction to the Site and the Excavations	58
4.2 The LBA and IA Glasses Analysed.....	60
4.2.1 HMK Glasses	61
4.3 Summary of HMK Samples.....	63
4.4 Base Glass Composition	63
4.5 Trace Elements.....	72
4.5.1 Rare Earth Elements (REE)	72
4.5.2 Sediment-Related Elements (SRE)	75
4.5.3 Alkali and Alkaline Earth Elements	76
4.5.4 Colourants and Opacifiers.....	77
4.6 General Conclusions	82
Chapter 5	84
Pella: Iron Age Glasses Results of Compositional Analyses	84
5.1 Introduction	84
5.2 Summary of LMLK Samples from Pella	84
5.3 LMLK Base Glass Composition	84
5.3.1 Summary.....	89
5.4 Trace Elements.....	90
5.4.1 Rare Earth Elements (REE)	90
5.4.2 Sediment-Related Elements (SRE)	91
5.4.3 Alkali and Alkaline Earth Elements	94
5.4.4 Colourants and Opacifiers.....	95
5.5 General Conclusions	97
Chapter 6	98
Nimrud: Iron Age Glasses Results Of Compositional Analyses Part 1	98
6.1 Introduction	98
6.2 The Site	99
6.2.1 The Excavations	99
6.2.2 The Glass	100
6.2.3 Summary of Samples	101
6.3 Base Glass Composition	101
6.3.1 Group 1.....	101
6.3.2 Group 2 and Ungrouped	106
6.3.3 Group 3.....	107
6.3.4 Group 4.....	107
6.3.5 Summary.....	110
6.4 Trace Element Analyses (Groups 1 to 3)	111
6.4.1 Rare Earth Elements (REE)	111
6.4.1.1 Group 1.....	113
6.4.1.2 Group 2.....	114

6.4.1.3 Group 3.....	114
6.4.1.4 Groups 1 to 3 Comparisons	114
6.4.2 Sediment-Related Elements (SRE)	117
6.4.3 Alkali and Alkaline Earth Elements	121
6.4.4 Colourants, Decolourants and Opacifiers	125
6.4.4.1 Pink/Purple and Colourless Glasses.....	127
6.4.4.2 Light Blue Translucent Glasses	128
6.4.4.3 Turquoise Opaque Glasses	129
6.5 General Conclusions.....	131
Chapter 7	133
Nimrud: Iron Age Glasses Results Of Compositional Analyses Part 2	133
7.1 Introduction: Cobalt Blue Glasses	133
7.2 Rare Earth Elements (REE)	133
7.3 Sediment-Related Elements (SRE)	136
7.4 Alkali and Alkaline Earth Elements	139
7.5 Colourant and Related Elements.....	141
7.6 General Conclusions.....	147
Chapter 8	148
Late Bronze Age Glasses - Comparisons and Interpretations	148
8.1 Introduction	148
8.2 LBA Glasses	148
8.2.1 Composition	148
8.2.2 The LBA Context: Chronological Considerations	149
8.3 Inter-Site Comparisons.....	149
8.3.1 Near Eastern Glasses.....	149
8.3.2 Egyptian New Kingdom Glasses	150
8.3.3 Comparisons of Trace Element Compositions	153
8.3.3.1 Cr, La, Zr, Ti and Iron Oxide	156
8.3.3.2 Li, Be, Sr and Cs.....	159
8.4 High- and Low-Lime Groups in LBA Glasses.....	162
8.4.1 Introduction	162
8.4.2 The Source of Lime in Ancient HMK Glasses.....	162
8.4.3 High- and Low-Lime Glasses from LBA Pella and Nuzi.....	163
8.4.4 The Relationship of Lime to Other Oxides and to Sr	167
8.4.5 Statistical Significance of Oxide Contents of the High- and Low-Lime Glasses	170
8.5 Conclusions.....	172
Chapter 9	174
Iron Age Glasses – Comparisons and Interpretations	174
9.1 Introduction	174
9.2 IA Base Glass Compositions	174
9.3 Trace Element Compositions.....	176
9.4 Regional Discriminants.....	177
9.5 An Emerging Technology	182
9.6 Iron Black Glasses	183
9.6.1 Chromite	185
9.7 Co Blue Glasses.....	186
9.7.1 Compositional Comparisons of Co blue Glasses	187
9.7.2 Raw Materials from Egypt in the Third Intermediate Period	194
9.7.3 Phoenician Traders	195
9.8 Colourless Glasses.....	197
Chapter 10.....	199
Conclusions and Future Research.....	199
10.1 Conclusions: LBA Glass-making.....	199
10.2 Conclusions: IA Glass-making.....	200
10.3 Future Research	201

Chapter 11	203
Epilogue: Published Research 2009-2019	203
11.1 Introduction	203
11.2 New and Consolidated Studies	203
11.3 Calcium Antimonate Opacification.....	204
11.4 Cobalt Colourants	205
11.4.1 Late Bronze Age	205
11.4.2 Iron Age.....	205
11.5 Trade and Provenance	206
11.5.1 Late Bronze Age	206
11.5.2 Iron Age.....	207
Conclusion	208
Bibliography 2009 – 2019	209
Bibliography	212
Appendix I	226
Model for Compositional Investigation of Ancient Glasses	226
Appendix II	228
NUZI: Results of Compositional Analyses (Chapter 3)	228
Appendix III	231
PELLA: Results of Compositional Analyses (Chapter 4)	231
Appendix IV	237
PELLA: Results of Compositional Analyses (Chapter 5)	237
Appendix V	241
NIMRUD: Results of Compositional Analyses (Chapters 6 and 7)	241
Appendix VI	248
EGYPT: Results of Compositional Analyses (Chapters 8 and 9)	248

List of Figures

Chapter 1

Figure 1-1 Map of the eastern Mediterranean region. Adapted from Tatton-Brown and Andrews 1991: 2.....	22
--	----

Chapter 2

Figure 2-1 Scanning electron micrograph of Pella sample 188, a turquoise opaque bead. Dark grey areas are weathered glass which form along microscopic cracks in the glass. White grains are the opacifying compound calcium antimonate. The scale bar represents ~1mm.	24
Figure 2-2 Scanning electron micrograph of Pella sample 79, from a turquoise bead opacified with calcium antimonate, visible as the white crystalline phase. The scale bar represents ~200µm.	25
Figure 2-3 Light micrograph of Pella sample 195 from a turquoise bead opacified with calcium antimonate, visible as white inclusions. Sample size is ~ 3mm across.	25
Figure 2-4 Scanning electron micrograph of Pella sample 55, a dark green glass, showing streams of small bubbles, several larger individual bubbles along the lower region, and four large dark grey silica grains which are incompletely melted and exhibit differential cooling cracks. The scale bar represents ~ 500 µm.....	25
Figure 2-5 Light micrograph of Pella sample 199 from a turquoise bead opacified with calcium antimonate. Streaks of less well opacified glass due to incomplete mixing or formation of the opacifier can be seen. Sample size is ~ 2.5 mm across.....	25
Figure 2-6 Light micrograph Pella 189 from a blue translucent bead. Bubbles are dispersed throughout the glass. Sample size is ~ 3mm across.	25
Figure 2-7 Light micrograph of Nimrud glass samples, cobalt wire (centre top) with a standard reference glass on either side, set in an epoxy resin stub, 25mm in diameter, and polished for SEM-EDS analysis.	26
Figure 2-8 Photograph of Nuzi glass samples with standard reference glass (centre) set in a pre-prepared epoxy resin stub, 20mm in diameter, and polished for EPMA analysis.	26

Chapter 3

Figure 3-1 Satellite map showing location of Nuzi between the Tigris River and the River Zab, in ancient Mesopotamia (modern Iraq), adapted from Google Earth.	38
Figure 3-2 Plan of city of Nuzi, adapted from Starr (1939), Plan 2, highlighting the size and position of the Temple and Palace, where most of the glass was found.	39
Figure 3-3 Plan of Temple A and immediate environs. Most of the glass was found in G29 and G50. Adapted from Starr (1939), Plan 13.	41
Figure 3-4 Nuzi 1930.66.90 half turquoise cylinder bead (diameter 12 mm)	42
Figure 3-5 Nuzi 1930.82.10 blue translucent vessel fragment (thickness 3 mm).....	42
Figure 3-6 Nuzi 1930.82.55 blue translucent vessel? Fragment (thickness ~4 mm)	43
Figure 3-7 Scatter plot of magnesia vs potash in wt% oxide for Nuzi glasses. * indicates reduced composition in this and all following plots.....	44
Figure 3-8 Scatter plot of alumina vs iron in wt% oxide for Nuzi glasses.	45
Figure 3-9 Scatter plot of lime vs magnesia in wt% oxide for Nuzi glasses.	45
Figure 3-10 Scatter plot of magnesia vs potash in wt% oxide for high- and low-lime groups of Nuzi glass showing a powerful positive correlation in the low-lime group and no correlation in the high-lime group.....	46
Figure 3-11 Line plot of the REE of individual Nuzi glasses (sample numbers given) showing similarity of pattern. A logarithmic scale was used. Data are normalised to MUQ.	47
Figure 3-12 Line plot of averaged REE from Nuzi glass. Data are normalised to MUQ. A logarithmic scale is used.....	48
Figure 3-13 Line plot of averaged Nuzi REE data and MUQ REE data both normalised to average chondrites for comparison (chondrite data from Sun and McDonough (1989), reproduced in Table 27 of Normalisers)	48
Figure 3-14 Line plot of the averaged REE normalised to MUQ for high- and low-lime groups.....	49
Figure 3-15 Line plot of the averaged concentrations of sediment-related trace elements in Nuzi glasses, normalised to MUQ. A logarithmic scale is used. Mo is not plotted as there is no MUQ value by which to normalise it. The dotted line crosses the Y-axis at 0.05 to represent the SBS of the Nuzi glasses as inferred from the REE concentrations.	50
Figure 3-16 Line plot of raw Nuzi sediment-related trace element data in ppb compared with MUQ on a logarithmic scale.	51
Figure 3-17 Line plot comparing averaged raw concentrations of sediment-related trace elements in the high and low lime groups. A logarithmic scale is used. Calculation of averages for W omits sample 28 and for Tl omits sample 26 because they are outliers.	51
Figure 3-18 Line plot of averaged raw data for Nuzi alkali and alkaline earth elements compared with MUQ. Note logarithmic scale.....	52
Figure 3-19 Line plot of averaged Nuzi alkali and alkaline earth trace elements normalised to MUQ, on a logarithmic scale. The dotted line represents the approximate sedimentary background signal as determined by the ratios of Nuzi REE to MUQ REE, at 0.05.....	52
Figure 3-20 Line plot of averaged raw data for low- and high-lime groups of Nuzi glass. A logarithmic scale is used.....	53
Figure 3-21 Line plot of averaged raw colourant and related elements in Nuzi opaque and translucent glasses, and MUQ, from ICP-MS data. A logarithmic scale is used to avoid compression. There is no MUQ value for Sb and Cd.	54
Figure 3-22 Scatter plot of Cu vs Sn in ppm for Nuzi glasses, excluding sample 16 which has an exceptionally high Sn content.	55
Figure 3-23 Scatter plot of Pb vs Ni for Nuzi glasses.	56

Figure 3-24 Line plot comparing averaged raw data for colourant elements in high- and low-lime glasses.....	56
Figure 3-25 Scatter plot of CaO* vs Sb for Nuzi glasses.....	57

Chapter 4

Figure 4-1 Satellite map showing position of Pella in the north Jordan valley, reproduced from Google Earth.....	58
Figure 4-2 Contour map of site of Pella indicating excavation areas referred to in text. Reproduced courtesy of the Pella Excavation Project.....	59
Figure 4-3 Three phases of the Migdol Temple, Area XXXII, showing the location in the Holy of Holies of two important LBA glass objects, an ingot (sample 86) and a disk pendant (not sampled). Plans adapted from Bourke 2004: Fig. 3.....	59
Figure 4-4 Plan of Tomb 62, in Area XI, adapted from Potts <i>et al.</i> 1985: 193.....	60
Figure 4-5 Plan of Tomb 89, in Area II. Adapted from a plan provided courtesy of the Pella Excavation Project. Red Xs mark the positions in which the glasses were found.....	60
Figure 4-6 Pella 190083 blue translucent tetrahedral ingot (Image courtesy of the Pella Excavation Project).....	63
Figure 4-7 Pella 990598 turquoise opaque pendant disc with lug (Image courtesy of the Pella Excavation Project).....	63
Figure 4-8 Pella 70746 blue translucent annular bead.....	64
Figure 4-9 Pella 70579D turquoise opaque annular bead.....	64
Figure 4-10 Pella 70505 turquoise opaque biconical bead.....	64
Figure 4-11 Pella 70845 blue translucent pinhead showing fresh glass under weathered surface.....	64
Figure 4-12 Pella 70948 turquoise opaque annular bead.....	65
Figure 4-13 Pella 70833 pale turquoise opaque annular bead.....	65
Figure 4-14 Pella 70843 turquoise opaque flattened spherical bead.....	65
Figure 4-15 Pella 70342 blue translucent barrel bead.....	65
Figure 4-16 Pella 70491 blue translucent biconical bead.....	66
Figure 4-17 Pella 70483 blue translucent spacer bead.....	66
Figure 4-18 Pella 70391 turquoise opaque annular bead.....	67
Figure 4-19 Pella 70355D turquoise opaque spacer bead (end view showing unweathered core).....	67
Figure 4-20 Scatter plot of magnesia vs potash (wt% oxide) for the Pella HMK glasses compared with the Nuzi HMK glasses showing similar oxide concentrations from both sites. Note that the correlation between the concentrations of the oxides is strong for the Nuzi glasses but not for the Pella glasses.....	68
Figure 4-21 Scatter plot of alumina vs iron (wt % oxide) with three outliers removed revealing a strong correlation between these oxides, though it is not as strong as is found in the Nuzi glasses. The rectangular outline represents the range in which the Nuzi glasses plot for comparison, revealing the greater range in concentration of both oxides found in the Pella HMK glasses.....	69
Figure 4-22 Scatter plot of lime vs magnesia (wt % oxide) for Nuzi and Pella HMK glasses showing the existence at both sites of the same two lime-related groups.....	70
Figure 4-23 Scatter plot of lime vs magnesia (wt % oxide) for opaque and translucent Pella HMK glasses.....	70
Figure 4-24 Scatter plot of magnesia vs potash (wt % oxide) for high and low lime groups of the Pella HMK glasses showing a lack of correlation in both, contrary to the good correlation found in the low-lime group of glasses from Nuzi (section 3.2).....	71
Figure 4-25 Line plot of the REE of individual Pella HMK glasses showing general similarity of pattern. A logarithmic scale is used. Data are normalised to MUQ.....	72
Figure 4-26 Line plot comparing averaged Pella HMK REE data and MUQ REE data both normalised to average chondrites for comparison (chondrite data from Sun and McDonough 1989, reproduced in Table 27).....	73
Figure 4-27 Line plot of the averaged translucent and opaque glass REE from Pella HMK glasses compared with those from Nuzi glasses. Data are normalised to MUQ. A logarithmic scale is used.....	73
Figure 4-28 Line plot of the averaged concentrations of sediment-related trace elements in Pella HMK glasses, normalised to MUQ. A logarithmic scale is used. Mo is not plotted as there is no MUQ value by which to normalise it. The dotted line crosses the Y-axis at 0.05 to represent the approximate SBS of the Pella HMK glasses.....	75
Figure 4-29 Line plot comparing averaged raw concentrations of sediment-related trace elements in opaque and translucent Pella HMK glasses with MUQ. A logarithmic scale is used.....	75
Figure 4-30 Line plot of averaged raw data for Pella HMK alkali and alkaline earth elements compared with MUQ. A logarithmic scale is used.....	77
Figure 4-31 Line plot of averaged Pella HMK alkali and alkaline earth trace elements normalised to MUQ, on a logarithmic scale. The dotted line represents the approximate SBS of 0.05, as determined by the ratios of Pella HMK REE to MUQ REE.....	77
Figure 4-32 Line plot of averaged raw data for opaque (high lime) and translucent (low lime) Pella HMK glasses. A logarithmic scale is used.....	78
Figure 4-33 Scatter plot of Cu vs Sn in ppm for Pella HMK and Nuzi glasses. Three glasses with exceptionally high Sn concentrations were removed to avoid compression of the graph.....	80
Figure 4-34 Line plot of colourant and related elements in Pella opaque and translucent glasses, and MUQ, from ICP-MS data. A logarithmic scale is used to avoid compression. There is no MUQ value by which to normalise Sb, Cd or As.....	80
Figure 4-35 Scatter plot of Cu vs As for Pella HMK glasses in ppm.....	81
Figure 4-36 Scatter plot of Co vs As for Pella HMK glasses divided into low and high As groups. Two high Co outliers (samples 189 and 207) are omitted from the low As group.....	81

Chapter 5

Figure 5-1 Pella 100231 green-black spherical bead, 7 mm L.....	84
---	----

Figure 5-2 Pella 100231 green-black small barrel bead.....	85
Figure 5-3 Pella 100231 green-black small barrel bead side view, 10 mm L.....	85
Figure 5-4 Pella 100147 green-black small barrel bead, 8 mm L.....	85
Figure 5-5 Scatter plot of magnesia vs potash in wt% oxide for Pella LMLK and HMHK groups, with Nuzi HMHK glass added for comparison.	86
Figure 5-6 Scatter plot of lime vs magnesia for Pella LMLK glasses compared with Pella HMHK glasses.....	86
Figure 5-7 Scatter plot of soda vs potash in wt% oxides for Pella HMHK and LMLK glasses, with Nuzi HMHK glass added for comparison.	87
Figure 5-8 Backscattered SEM image of IA black glass, PEL 132B. White inclusions are chromite (the largest are indicated by arrows). Large gray inclusions are silica and a zone of small grains of a pyroxenoid devitrification product may be seen at the top of the micrograph.	88
Figure 5-9 Scatter plot of iron vs alumina in wt% oxides for Pella LMLK and HMHK groups.	88
Figure 5-10 Line plot of the REE of individual Pella LMLK glasses showing similarity of pattern and concentration. A logarithmic scale is used. Data are normalised to MUQ.	89
Figure 5-11 Line plot comparing averaged Pella LMLK and HMHK REE data with MUQ REE data, all normalised to average chondrites for comparison (chondrite data are reproduced in Table 27).	90
Figure 5-12 Line plot of averaged REE from Pella HMHK and LMLK glasses. Data are normalised to MUQ. A logarithmic scale is used.	91
Figure 5-13 Line plot of the averaged concentrations of sediment-related trace elements in Pella HMHK and LMLK glasses, normalised to MUQ. A logarithmic scale is used. Mo is not plotted as there is no MUQ value by which to normalise it. Dotted lines cross the Y-axis at 0.25 to represent the SBS of the Pella LMLK glasses, and at 0.05 for the SBS of the HMHK glasses.	92
Figure 5-14 Line plot of raw Pella sediment-related trace element data in ppb for HMHK and LMLK glasses, compared with MUQ, on a logarithmic scale.	92
Figure 5-15 Line plot of averaged Pella alkali and alkaline earth trace elements normalised to MUQ, on a logarithmic scale. Dotted lines cross the Y-axis at 0.25 to represent the SBS of the Pella LMLK glasses, and at 0.05 for the SBS of the HMHK glasses.	94
Figure 5-16 Line plot of averaged raw data for Pella LMLK alkali and alkaline earth elements compared with Pella HMHK and MUQ. A logarithmic scale is used.	94
Figure 5-17 Scatter plot of iron oxide vs Ni for Pella LMLK glasses.	95
Figure 5-18 Line plot of raw averaged colourant and related elements in Pella LMLK and HMHK glasses compared with MUQ, from ICP-MS data. A logarithmic scale is used. There is no MUQ value by which to normalise As, Sb or Cd.	96

Chapter 6

Figure 6-1 Satellite map showing location of Nimrud on the east bank of the Tigris River, in relation to Nuzi and Pella, from Google Earth.	97
Figure 6-2 Contour map of the mound or acropolis showing the positions of excavated buildings (1957) from which much of the glass analysed in this study was unearthed. Reproduced from Mallowan (1966: 32).	98
Figure 6-3 Plan of Fort Shalmaneser, located in the south-east corner of the site. Reproduced from Mallowan (1966).	99
Figure 6-4 Nimrud N.785 91574 dark blue opaque beard fragment.....	101
Figure 6-5 Nimrud turquoise opaque ingot fragment.....	102
Figure 6-6 Nimrud 1994-11-5, 234 ND12, 541 light blue translucent vessel fragment.....	103
Figure 6-7 Examples of Group 4 cobalt blue inlays, various sizes.....	103
Figure 6-8 Nimrud 1994-11-5, 67 ND4138 dark blue opaque beard fragment.....	104
Figure 6-9 Scatter plot of magnesia vs potash in wt% oxide for Nimrud glasses.	106
Figure 6-10 Scatter plot of magnesia vs potash in wt% oxide comparing Brill's (1999b) analyses of Nimrud glasses with those of the current study (yellow and red glasses not plotted).	107
Figure 6-11 Scatter plot of alumina vs iron in wt% oxide for Nimrud Groups 1-3 and ungrouped glasses. Group 4 glasses are plotted separately as alumina is more concentrated.....	108
Figure 6-12 Scatter plot of alumina vs iron in wt% oxide illustrating clearly the difference between the cobalt coloured blue glasses of Group 4 and the other Nimrud glasses.....	109
Figure 6-13 Scatter plot of lime vs alumina for all Nimrud glasses in wt% oxide.	109
Figure 6-14 Scatter plot of magnesia vs alumina in wt% oxides for Nimrud Group 4 glasses.....	110
Figure 6-15 Line plot of the REE of individual Nimrud Group 1 glasses showing similarity of pattern and concentration. A logarithmic scale is used. Data are normalised to MUQ.	112
Figure 6-16 Line plot of the REE of individual Nimrud Group 2 and ungrouped glasses showing similarity of pattern and concentration. A logarithmic scale is used. Data are normalised to MUQ.	112
Figure 6-17 Line plot of the REE of individual Nimrud Group 3 glasses showing variability of pattern at relatively similar concentrations. A logarithmic scale is used. Data are normalised to MUQ.	113
Figure 6-18 Scatter plot of alumina vs Yb for Nimrud Groups 1 to 3 glasses.	114
Figure 6-19 Line plot of averaged REE from Nimrud glasses. Data are normalised to MUQ. Note logarithmic scale.....	114
Figure 6-20 Line plot of averaged Nimrud REE data for glass Groups 1 to 3, and MUQ. Data are normalised to average chondrites for comparison (see Table 27).	115
Figure 6-21 Line plot of averaged REE data from Nimrud Groups 1 to 3 glasses compared with Nuzi HMHK glass REE. Data are normalised to MUQ. Note logarithmic scale.	115
Figure 6-22 Line plot of averaged concentrations of sediment-related trace elements in Nimrud Group 1 glasses, normalised to MUQ. A logarithmic scale is used. Mo is not plotted as there is no MUQ value by which to normalise it. The dotted line crosses the Y-axis at 0.1 to represent the SBS of Group 1 glasses.	116

Figure 6-23 Line plot of averaged concentrations of sediment-related trace elements in Nimrud Group 2 glasses, normalised to MUQ. A logarithmic scale is used. The dotted line crosses the Y-axis at 0.08 to represent the SBS of the Group 2 glasses.	118
Figure 6-24 Line plot of averaged concentrations of sediment-related trace elements in Nimrud Group 3 glasses, normalised to MUQ. A logarithmic scale is used. The dotted line crosses the Y-axis at 0.04 to represent the SBS of the Group 3 glasses.	118
Figure 6-25 Line plot of raw Nimrud Groups 1 to 3 sediment-related element data in ppb compared with MUQ on a logarithmic scale.....	119
Figure 6-26 Scatter plot of Ti vs Nb in ppb for Nimrud Groups 1- 3 glasses.....	119
Figure 6-27 Scatter plot of Ti vs Zr in ppb for Nimrud Groups 1 to 3 and ungrouped glasses.....	120
Figure 6-28 Scatter plot of Hf vs Zr in ppb for Nimrud Groups 1 to 3 and ungrouped glasses.....	120
Figure 6-29 Line plot comparing Nimrud sediment-related elements in plant ash glasses (Groups 1 and 2) with typical 2nd millennium BC HMK glasses from Nuzi. Data are normalised to MUQ. A logarithmic scale is used.	121
Figure 6-30 Line plot of averaged raw data for Nimrud alkali and alkaline earth elements compared with MUQ. Note the logarithmic scale.....	122
Figure 6-31 Line plot of data averaged and normalised to MUQ for Nimrud Group 1. The dotted line represents the SBS level of 0.1	122
Figure 6-32 Line plot of data averaged and normalised to MUQ for Nimrud Group 2. The dotted line represents the SBS level of 0.08.....	123
Figure 6-33 Line plot of data averaged and normalised to MUQ for Nimrud Group 3. The dotted line represents the SBS level of 0.04.....	123
Figure 6-34 Line plot of data averaged and normalised to MUQ for Nuzi glasses. The dotted line represents the SBS level of 0.05.	124
Figure 6-35 Line plot of data averaged and normalised to MUQ for Pella HMK glasses. The dotted line represents the SBS level of 0.05.	124
Figure 6-36 Line plot of raw data for colourant and related elements for individual Nimrud pink/purple and colourless glasses. A logarithmic scale is used.....	127
Figure 6-37 Line plot of raw data for colourant and related elements for individual Nimrud light blue translucent glasses. A logarithmic scale is used.....	127
Figure 6-38 Line plot of raw data for colourant and related elements for individual Nimrud turquoise opaque glasses. A logarithmic scale is used.....	128
Figure 6-39 Line plot of averaged raw data for Nimrud colourant and related elements and MUQ, from ICP-MS data. A logarithmic scale is used. There is no MUQ value for Sb and Cd.	129
Figure 6-40 Line plot of averaged raw Nimrud Cu blue glass colourant and opacifier related trace element data compared with similarly coloured Pella glasses. A logarithmic scale is used.....	129

Chapter 7

Figure 7-1 Line plot of the REE of individual Nimrud Group 4A glasses. A logarithmic scale is used. Data are normalised to MUQ.....	133
Figure 7-2 Line plot of the REE of individual Nimrud Group 4B glasses. A logarithmic scale is used. Data are normalised to MUQ.....	133
Figure 7-3 Scatter plot of Eu/Yb vs Co in ppb for Nimrud Group 4 glasses.....	134
Figure 7-4 Line plot of averaged REE from Nimrud Groups 4A and 4B glasses compared with Group 2 Co blue glass 5BM. Data are normalised to MUQ. A logarithmic scale is used.	134
Figure 7-5 Line plot of averaged Nimrud REE data for Groups 4A and 4B glasses. Data are normalised to average chondrites for comparison (Table 27).....	135
Figure 7-6 Line plot of raw Nimrud Group 4 sediment-related element data in ppb compared with MUQ on a logarithmic scale.....	136
Figure 7-7 Line plot of averaged concentrations of sediment-related trace elements in Nimrud Group 4 glasses, normalised to MUQ. A logarithmic scale is used. The dotted line crosses the Y-axis at 0.07 to represent the approximate SBS of the Group 4 glasses.	136
Figure 7-8 Line plot of averaged sediment-related element data for Nimrud Groups 1 – 4 glasses. Data are normalised to MUQ. A logarithmic scale is used.....	137
Figure 7-9 Line plot of averaged sediment-related trace element data for Nimrud LMLK glasses compared with Pella LMLK glasses. Data are normalised to MUQ. A logarithmic scale is used.....	137
Figure 7-10 Scatter plot of Li vs Rb for Nimrud Group 4 glasses in ppb.	139
Figure 7-11 Scatter plot of lime vs Sr for Nimrud Group 4 glasses.	139
Figure 7-12 Line plot of raw alkali and alkaline earth element data for Nimrud Groups 3 and 4 mineral soda glasses and MUQ. A logarithmic scale is used.....	140
Figure 7-13 Line plot of averaged alkali and alkaline earth element data for Nimrud Groups 3 and 4, and Pella LMLK glasses. Data are normalised to MUQ. A logarithmic scale is used.....	140
Figure 7-14 Line plot of data averaged and normalised to MUQ for Nimrud Group 4. The dotted line represents the SBS of approximately 0.07.....	141
Figure 7-15 Scatter plot of Cu vs Co for Group 4 blue glasses.....	142
Figure 7-16 Scatter plot of Co vs Ni in ppm for Group 4 blue glasses.	143
Figure 7-17 Scatter plot of Co vs Zn in ppm for Group 4 blue glasses.....	143
Figure 7-18 Scatter plot of Co vs magnesia for Group 4 blue glasses.....	143
Figure 7-19 Scatter plot of Co vs alumina for Group 4 blue glasses.	144
Figure 7-20 Scatter plot of Co vs manganese for Group 4 blue glasses.....	144

Figure 7-21 Scatter plot of Sb vs Pb in ppm for Group 4 blue glasses. Samples 29P and 4BMA are omitted as they have extremely high levels of Pb.	145
Figure 7-22 Scatter plot of Sb vs Co in ppm for Group 4 blue glasses.	145
Figure 7-23 Line plot of raw colourant-related trace element data for Nimrud Group 4 blue glasses compared with MUQ. A logarithmic scale is used. There are no MUQ values for Cd and Sb.	146

Chapter 8

Figure 8-1 Scatter plot of magnesia vs potash for LBA HMHK glasses from Nuzi ($n=46$), Pella ($n=43$), Tell al-Rimah ($n=1$), and Tell Brak ($n=35$). Sources cited in text.	149
Figure 8-2 Scatter plot of lime vs magnesia for LBA HMHK glasses from Nuzi ($n=46$), Pella ($n=43$), Tell al-Rimah ($n=1$), and Tell Brak ($n=35$). Sources cited in the text.	149
Figure 8-3 Scatter plot of magnesia vs potash for LBA HMHK Egyptian and Near Eastern glasses. Sources cited in text. Co blue glasses are excluded.	150
Figure 8-4 Scatter plot of lime vs magnesia for LBA HMHK Egyptian and Near Eastern glasses. Sources cited in text. Co blue glasses are excluded.	151
Figure 8-5 Scatter plot of soda vs potash for LBA HMHK Egyptian and Near Eastern glasses. Sources cited in text. Co glasses are excluded.	151
Figure 8-6 Scatter plot of silica vs alumina for LBA HMHK Egyptian and Near Eastern glasses. Sources cited in text. Co glasses are excluded.	152
Figure 8-7 Scatter plot of alumina vs iron oxide for LBA HMHK Egyptian and Near Eastern glasses. Egyptian glasses are from Amarna and Malkata analysed by Shortland and Eremin (2006: 584-588). Nuzi and Tell Brak glasses analysed by Shortland and Eremin (2006: 594-595) are combined with analyses of Pella and Nuzi glasses from the present study. Only analyses which give data for FeO are included. Co blue glasses are excluded.	152
Figure 8-8 Line and dot plot of SRE data for glasses from Nuzi analysed by Shortland <i>et al.</i> (2007: 784) (Nuzi AS) and analysed in the present study (Nuzi).	153
Figure 8-9 Line and dot plot of SRE data for glasses from Egypt and the Near East. Data for Egypt and Tell Brak from Shortland <i>et al.</i> (2007: 784-785) and for Nuzi and Pella from the present study.	154
Figure 8-10 Line and dot plot of alkali and alkaline earth element data for glasses from Nuzi (Nuzi AS) analysed by Shortland <i>et al.</i> (2007: 784) and for glasses (Nuzi) analysed in the present study.	154
Figure 8-11 Line and dot plot of alkali and alkaline earth element data for glasses from Egypt and the Near East. Data for Egypt and Tell Brak from Shortland <i>et al.</i> (2007: 784-785) and for Nuzi and Pella from the present study.	155
Figure 8-12 Scatter plot of iron oxide vs Ti for Near Eastern and Egyptian glasses. Data sources cited in the text.	156
Figure 8-13 Scatter plot of Zr/Ti vs Cr/La for LBA Near Eastern (squares) and Egyptian (triangles) glasses. Data for Egypt, Nuzi and Tell Brak from Shortland <i>et al.</i> (2007: 784-785) and for Nuzi and Pella from the present study. This scatter plot is of the type introduced by Shortland <i>et al.</i> (2007).	157
Figure 8-14 Scatter plot of Zr vs Cr/La for LBA Near Eastern (squares) and Egyptian (triangles) glasses. Data for Egypt, Nuzi and Tell Brak from Shortland <i>et al.</i> (2007: 784-785) and for Nuzi and Pella from the present study.	157
Figure 8-15 Scatter plot of Be vs Li for LBA Near Eastern (squares) and Egyptian (triangles) glasses. Data for Egypt, Nuzi and Tell Brak from Shortland <i>et al.</i> (2007: 784-785) and for Nuzi and Pella from the present study.	158
Figure 8-16 Scatter plot of Sr vs Cs for LBA Near Eastern (squares) and Egyptian (triangles) glasses. Data for Egypt, Nuzi and Tell Brak from Shortland <i>et al.</i> (2007: 784-785) and for Nuzi and Pella from the present study.	159
Figure 8-17 Scatter plot of Sr/Cs vs Cs for LBA Near Eastern (squares) and Egyptian (triangles) glasses. Data for Egypt, Nuzi and Tell Brak from Shortland <i>et al.</i> (2007: 784-785) and for Nuzi and Pella from the present study.	159
Figure 8-18 Scatter plot of Sr/Cs vs Li/Be for LBA Near Eastern (squares) and Egyptian (triangles) glasses. Data for Egypt, Nuzi and Tell Brak from Shortland <i>et al.</i> (2007: 784-785) and for Nuzi and Pella from the present study.	160
Figure 8-19 Scatter plot of Li/Be vs Cr/La for LBA Near Eastern (squares) and Egyptian (triangles) glasses. Data for Egypt, Nuzi and Tell Brak from Shortland <i>et al.</i> (2007: 784-785) and for Nuzi and Pella from the present study.	161
Figure 8-20 Histogram illustrating the bimodal distribution of samples in half per cent increments over the range of lime (CaO^*) concentrations measured in wt % of 44 Nuzi glasses analysed by Shortland (2006: 595), Brill (1999b: 40-41) and samples analysed in the present study.	163
Figure 8-21 Histogram illustrating the bimodal distribution of samples in half per cent increments over the range of lime (CaO^*) concentrations measured in wt% of 43 Pella HMHK glasses analysed in the present study.	163
Figure 8-22 Scatter plot of lime vs Sb for Pella HMHK blue glasses. The low Sb opaque glass is sample 209, the low-lime opaque glass is sample 222, and the high-lime translucent glass is sample 194.	164
Figure 8-23 Histogram illustrating the bimodal distribution of samples in half per cent increments over the range of lime (CaO^*) concentrations measured in wt% of 124 Near Eastern glasses. Nuzi glasses $n=46$, Pella glasses $n=43$, Tell Brak glasses $n=35$. Sources cited in the text.	165
Figure 8-24 Histogram illustrating the distribution of samples in half per cent increments over the range of lime (CaO^*) concentrations measured in wt% of 283 Egyptian HMHK glasses. Sources cited in the text. Although Lisht glasses and some pre-Malkata glasses have lower average lime contents than other Egyptian glasses, there is some overlap between the ranges of concentrations for these and other Egyptian glasses, which forms the continuum of lime concentrations plotted in this figure.	165
Figure 8-25 Scatter plot of lime vs Sr for high- and low-lime glasses from Nuzi, represented by the combined data for 28 samples from Shortland and Eremin (2006: 595) and the present study.	167
Figure 8-26 Scatter plot of lime vs Sr for LBA high- and low-lime glasses from Pella, from the present study.	167
Figure 8-27 Histogram comparing the concentrations in wt% oxides of plant ash associated elements in the high and low lime groups at Nuzi. Data for these oxides are re-summed to 100%.	168
Figure 8-28 Histogram comparing the concentrations in wt% oxides of plant ash associated elements in the high and low lime groups of Pella HMHK glasses. Data for these oxides are re-summed to 100%.	168

Chapter 9

Figure 9-1 Scatter plot of soda vs lime for IA glasses from the Near East and Egypt. Data for Nesikhons' glass from Schlick-Nolte and Werthmann (2003: 26). Pella and Nimrud data are from the present study.	174
Figure 9-2 Scatter plot of magnesia vs potash for low potash IA glasses from the Near East and Egypt. Data for Nesikhons' glass from Schlick-Nolte and Werthmann (2003: 26). Pella and Nimrud data are from the present study....	174
Figure 9-3 Histogram comparing the bimodal distribution of lime in Nuzi HMK glasses with the lime contents of Group 1 and Group 2 HMK glasses from Nimrud using data from Brill 1999b (Nuzi and Nimrud), Shortland and Eremin 2006 (Nuzi) and the present study (Nuzi and Nimrud).....	175
Figure 9-4 Histogram comparing the concentrations of plant ash associated elements in typical 2nd millennium glasses from Nuzi and Nimrud 1st millennium plant ash glasses. Data for these oxides are re-summed to 100%.	176
Figure 9-5 Scatter plot of Zr/Ti vs Cr/La for IA Near Eastern glasses from Nimrud and Pella compared with LBA HMK glasses from Pella and LBA Egyptian glasses of both HMK and Co blue low potash glasses. Data sources are cited in the text.....	177
Figure 9-6 Scatter plot of Zr vs Cr/La for IA Near Eastern glasses from Nimrud and Pella compared with LBA HMK glasses from Pella and LBA Egyptian glasses of both HMK and Co natron-type glasses. Data sources are cited in the text.....	178
Figure 9-7 Scatter plot of Sr vs Cs for IA glasses from Pella and Nimrud compared with LBA glasses from Pella and Egypt. All non-Egyptian data are from the present study. Egyptian data from Shortland <i>et al.</i> (2007) and analyses of the author (Appendix VI).....	179
Figure 9-8 Scatter plot of Sr/Cs vs Li/Be for IA glasses from Pella and Nimrud compared with LBA glasses from Pella and Egypt. All non-Egyptian data are from the present study. Egyptian data are from Shortland <i>et al.</i> (2007) and analyses of the author (Appendix VI).	180
Figure 9-9 Scatter plot of FeO vs Ti for Nimrud Groups 1 to 4 compared with LBA glasses from the Near East and Egypt. Data sources cited in the text.....	180
Figure 9-10 Scatter plot of magnesia vs potash for iron black glasses from Hasanlu, France and Pella of the early 1st millennium BC compared with LBA Pella HMK glasses. Data sources cited in the text.	183
Figure 9-11 Scatter plot for soda vs lime for iron black glasses from Hasanlu, France and Pella of the early 1st millennium BC. Data sources cited in the text.....	183
Figure 9-12 Scatter plot of alumina vs magnesia for iron black glasses from Hasanlu, France and Pella of the early 1st millennium BC. Data sources cited in text.	184
Figure 9-13 Map of Egypt showing the locations of the Western Desert oases in relation to the Nile Valley and the Mediterranean coast. Adapted from Hendrickx and Vermeersch (2000: 22).	186
Figure 9-14 Diagram of the usage of Co to colour Egyptian and Mesopotamian glasses between the LBA and IA.	187
Figure 9-15 Scatter plot of magnesia vs potash for Co blue glasses from Nimrud, Egypt and France. Data sources are cited in the text.....	187
Figure 9-16 Scatter plot of alumina vs magnesia for Co blue glasses from Nimrud, Egypt and France. Data sources are cited in the text.....	188
Figure 9-17 Scatter plot of soda vs lime for Co blue glasses from Nimrud, Egypt and France. Data sources are cited in the text.....	188
Figure 9-18 Scatter plot of alumina vs Co for Co blue glasses from Nimrud, Egypt and France. Data sources are cited in the text.....	189
Figure 9-19 Scatter plot of Ni vs Co for Co blue glasses from Nimrud, Egypt and France. Data sources are cited in the text.....	190
Figure 9-20 Line and dot plot comparing the average REE concentrations for Nimrud Group 4 and Egyptian Co blue glasses. Data are normalised to MUQ.....	191
Figure 9-21 Line and dot plot comparing the averaged raw concentrations for SRE for Nimrud Group 4 and Egyptian Co blue glasses.	191
Figure 9-22 Line and dot plot comparing the averaged raw concentrations for alkali and alkaline earth elements for Nimrud Group 4 and Egyptian Co blue glasses.	192
Figure 9-23 Line and dot plot of the raw concentrations for colourant related elements for Nimrud Group 4 Co blue glasses.	192
Figure 9-24 Line and dot plot of the raw concentrations for colourant related elements for Egyptian Co blue glasses.	192
Figure 9-25 Line plot of averaged raw Nimrud colourless glass colourant and related trace element data compared with Pella colourless sample 119. A logarithmic scale is used.....	197

List of Tables

Chapter 2

Table 2-1 Analyses of standard glasses by SEM	28
Table 2-2 EPMA Analytical Protocol. All standards are from the JEOL Taylor Block	29
Table 2-3 Analyses of standard glasses by EPMA.....	30
Table 2-4 Elements measured by ICP-MS in the present study	31
Table 2-5 Minimum Detection Levels for ICP-MS analyses of glasses	31
Table 2-6 Elements detected by SEM-EDS and EPMA, giving oxide names used in the text, and indicating those that were also detected with ICP-MS.....	32
Table 2-7 MUQ and average chondrite elemental values (ppb) used by ACQUIRE for normalisation of ICP-MS data (Kamber et al. 2005; Sun and McDonough 1989).....	35
Table 2-8 MUQ values for normalisation of SEM and EPMA oxide data (Kamber <i>et al.</i> 2005)	35

Chapter 3

Table 3-1 Description and provenance of Nuzi glass samples.	42
Table 3-2 Average reduced compositions of 16 Nuzi glasses in wt% oxide.....	44
Table 3-3. Average reduced compositions of low- and high-lime Nuzi glasses in wt% oxide.....	46
Table 3-4 Average REE for Nuzi glasses in ppb.	47
Table 3-5. Averaged compositions in ppb of sediment-related elements from Nuzi glasses.....	50
Table 3-6. Average compositions in ppb of alkali and alkaline earth elements from Nuzi glasses.	52
Table 3-7 Averaged compositions of colourant and related elements from Nuzi glasses, presented in ppm.	54

Chapter 4

Table 4-1 Summary of glasses analysed from Pella in the LBA to IA.	61
Table 4-2 Description and provenance of Pella HMHK glass samples.	63
Table 4-3 Average reduced compositions of 43 Pella HMHK glasses in wt% oxide. Included here are 39 LBA and four IA HMHK glasses.	68
Table 4-4 Averaged, reduced concentrations of base glass oxides in low- and high-lime Pella HMHK glasses presented in wt%.	71
Table 4-5 Averaged raw values for Rare Earth Elements from Pella HMHK glasses in ppb.	72
Table 4-6 Averaged raw concentrations in ppb of sediment-related elements from Pella HMHK glasses.	74
Table 4-7 Averaged raw concentrations in ppb of alkali and alkaline earth elements from Pella HMHK glasses.	76
Table 4-8 Concentrations in ppm of colourant and related elements from Pella HMHK glasses.	78

Chapter 5

Table 5-1 Description and provenance of Pella LMLK glass samples.....	84
Table 5-2 Average reduced compositions of 23 Pella LMLK glasses in wt % oxide.	85
Table 5-3 Averaged raw values for Rare Earth Elements from Pella LMLK glasses in ppb.....	90
Table 5-4 Averaged compositions in ppb of sediment-related elements from Pella LMLK glasses.	91
Table 5-5 Average compositions in ppb of alkali and alkaline earth elements from Pella LMLK glasses.	93
Table 5-6 Compositions in ppm of colourant and related elements from Pella LMLK glasses.	95

Chapter 6

Table 6-1 Description of Nimrud glass samples divided into groups determined from base glass composition by SEM-EDS analyses.	101
Table 6-2 Average reduced compositions of 50 Nimrud glasses in wt% oxide.....	105
Table 6-3 Averaged raw values for Rare Earth Elements from Nimrud glasses, Groups 1 to 3 in ppb.	111
Table 6-4 Averaged concentrations in ppb of sediment-related elements from Nimrud Groups 1 to 3, and ungrouped glasses.....	117
Table 6-5 Average compositions in ppb of alkali and alkaline earth elements from Nimrud glasses Groups 1 to 3, and ungrouped glasses.....	121
Table 6-6 Compositions in ppm of colourant, opacifier and related elements from Nimrud Groups 1 to 3 glasses.....	125

Chapter 7

Table 7-1 Averaged raw values for Rare Earth Elements from Nimrud Group 4 glasses in ppb.	132
Table 7-2 Averaged concentration in ppb of sediment-related elements from Nimrud Group 4 glasses.....	135
Table 7-3 Average compositions in ppm of alkali and alkaline earth elements from Nimrud Group 4 glasses.....	138
Table 7-4 Average compositions in ppm of colourants and related trace elements from Nimrud cobalt coloured glasses.	142
Table 7-5 Cobalt blue Group 4 glasses classified as LCLC or HCHC.	142

Chapter 8

Table 8-1 Concentrations in ppm of Zr, Ti, Cr and La and ratios of Zr/Ti and Cr/La for glasses from the Near East and Egypt.	156
Table 8-2 Concentrations in ppm of Li, Be, Sr and Cs and the ratios of Li/Be and Sr/Cs for glasses from the Near East and Egypt.	158
Table 8-3 Average ratios of oxides in low- and high-lime glasses from Nuzi and Pella glass data from the present study ..	169
Table 8-4 Results of two-tailed unpaired t-tests for Nuzi and Pella high- and low-lime group oxide data.....	170

Chapter 9

Table 9-1 Average concentrations in ppm of Zr, Ti, Cr and La and ratios of Zr/Ti and Cr/La for glasses from the IA Near East and LBA Egypt.....177
Table 9-2 Averaged concentrations in ppm of Li, Be, Sr and Cs and ratios of Li/Be and Sr/Cs for glasses from the IA Near East and LBA Pella and Egypt.179

Appendix II

Table 1 Raw values NUZI base glass oxides (wt%)218
Table 2 Raw values NUZI rare earth elements (ppb)219
Table 3 Raw values for NUZI sediment-related elements (ppb)219
Table 4 Raw values for NUZI alkali and alkaline earth elements (ppb).....220
Table 5 Raw values for NUZI colourant and related elements (ppb).....220

Appendix III

Table 6 Raw values for PELLA HMKH base glass oxides (wt %).....221
Table 7 Raw values for PELLA HMKH rare earth elements (ppb)223
Table 8 Raw values for PELLA HMKH sediment-related elements (ppb).....224
Table 9 Raw values for PELLA HMKH alkali and alkaline earth elements (ppb).....225
Table 10 Raw values for PELLA HMKH colourant and related elements (ppb).....226

Appendix IV

Table 11 Raw values for PELLA LMLK base glass oxides (wt%)227
Table 12 Raw values for PELLA LMLK rare earth elements (ppb)228
Table 13 Raw values PELLA LMLK sediment-related elements (ppb)228
Table 14 Raw values for PELLA LMLK alkali and alkaline earth elements (ppb)229
Table 15 Raw values for PELLA LMLK colourant and related elements (ppb)230

Appendix V

Table 16 Raw values for NIMRUD base glass oxides (wt %)231
Table 17 Raw values for NIMRUD base glass oxides (wt %)233
Table 18 Raw values for NIMRUD rare earth elements (ppb)234
Table 19 Raw values for NIMRUD sediment-related elements (ppb)235
Table 20 Raw values for NIMRUD alkali and alkaline earth elements (ppb)237
Table 21 Raw values for NIMRUD colourant and related elements (ppb)238

Appendix VI

Table 22 Raw values for EGYPT base glass oxides (wt%)240
Table 23 Raw values for EGYPT rare earth elements (ppb)240
Table 24 Raw values for EGYPT sediment-related elements (ppb).....240
Table 25 Raw values for EGYPT alkali and alkaline earth elements (ppb).....241
Table 26 Raw values for EGYPT colourant and related elements (ppb).....241

Preface

This project arose from my intense interest in archaeology and human technological achievement, a combination of a fascination for history and for the chemistry of archaeological materials, which forms the essence of archaeological science. Rollinson (1993: ix) as a geochemist wrote,

‘what excuse have I as a single author for venturing into the fields of so many experts in an attempt to explain the methodologies of the main sub-disciplines of geochemistry? ...Today of course the problem is compounded, for geochemistry has a multitude of relatively new and comparatively narrow fields.’

The same can be said of a modern archaeological investigation into ancient technology, such as this one. The researcher is required to use a combination of related disciplines. There are experts in each field of scientific instrumental analysis, experts in geochemistry and its various subdivisions, those who specialise in glass chemistry, or in statistics, those whose field is archaeology, from regional and chronological studies to the classification of artefacts into typologies, the writing of history and the deciphering of ancient texts. Indeed, all of these aspects must be combined to produce a complete and well-informed work which contributes to knowledge and from which all who read it can derive useful information.

That such studies are now possible, even essential, to produce the highly detailed information required to solve archaeological problems that cannot be solved in traditional archaeological ways, is my defence for taking on such a task as an individual. Naturally, I have called on experts when possible, but take responsibility for compiling the whole into the dissertation as presented.

Moorey (1985: x) advocated the benefits of a combined approach to studying archaeological materials when he observed,

‘In this generation of proliferating information no single scholar can hope to combine the formidable

range of learning ideally required for a task of this kind. Still, ... it is much needed and, at a preliminary stage, there are distinct advantages in one scholar, rather than a team, undertaking it’.

Not only are there many aspects to the investigation of ancient glass which must be considered, but the very nature of glass itself contributes to the complexity of its study. The words of McCray and Kingery (1998: 2) describe this challenge well.

‘Glass, in comparison to other inorganic art/archaeological materials, might be said to represent “the worst of both worlds”. Glass does not have an easily characterized microstructure (except for opaque and some colored glasses) in the same manner as traditional ceramics or metals. Glass often does not retain evidence of its manufacture in the same manner that a metal’s microstructure “speaks” to a scholar. And glass does not have diagnostic features such as temper or inclusions that can help in ascertaining provenance in the way that pottery does. Indeed ... the extremely complicated business of interpreting glass compositions ... should be viewed as a challenge and opportunity to glass researchers rather than a bane.’

Glass researchers include both scientists and archaeologists, and many shades in between, but it has often been the case that scientists write in order to communicate with other scientists rather than archaeologists, and not all archaeologists make use of scientific analysis. It is hoped, while the core of the present work is essentially a scientific treatise, that it will satisfy both the scientifically and historically inclined, providing a synthesis of data and ideas into which the specialist will be able to delve more deeply at will, and from which future research will spring.

There are always more questions than answers.

Acknowledgements

I owe sincere thanks to the following people without whom this study would neither have started, nor been completed. I wish to express my whole-hearted appreciation to them.

My supervisors:

Daniel T. Potts, Edwin Cuthbert Hall Professor of Middle Eastern Archaeology at the University of Sydney (now Institute for the Study of the Ancient World, New York University), for his unfailing support and belief in me, which made the journey possible and sustained me throughout.

Ian C. Freestone, Deputy Keeper of the Department of Scientific Research at the British Museum (now Professor, Department of Archaeology, University College London), for his generous and patient guidance, unflagging good humour and keen insight for which I am deeply grateful. I am indebted to him for teaching me to operate an SEM, for analysing the glasses from Pella, for generously providing samples of Egyptian glasses for analysis and for the scanning electron micrographs that appear in this study. Thanks to Pam Freestone for her kind and patient hospitality.

Associate Professor Mike Barbetti, formerly Director of the NWG Macintosh Centre for Quaternary Dating at the University of Sydney, for his support and encouragement for this project, and for providing the opportunity for teaching and research. MB introduced me to the excellent analytical facility at the Advanced Centre for Queensland University Isotope Research Excellence (ACQUIRE) (now the Centre for Microscopy and Microanalysis) at the University of Queensland.

This study would not have been possible without the financial assistance from a University Postgraduate Award, two Near Eastern Archaeology Foundation grants-in-aid, the Catherine Southwell-Keely Travel Award, two Carlyle Greenwell bequests, the NWG Macintosh Centre for Quaternary Dating and three awards from the Postgraduate Research Support Scheme, all at the University of Sydney.

The following people and institutions for their time and for the opportunity to study and sample ancient glasses from their collections. Without them, this study could not have been made:

Dr James Armstrong, Harvard Semitic Museum, Boston, for access to the glasses from Nuzi and for allowing samples to be taken;

Dr St John Simpson, Assistant Keeper, and Dr Jonathan Tubb, Assistant Keeper, Department of the Middle East, the British Museum, for facilitating access to and sampling of the museum's collection of ancient glasses, principally those from Nimrud. Thanks to SJS for ongoing assistance with the study of the material from Nimrud;

Dr Stephen J. Bourke, Director of the University of Sydney Pella Project, and the Sar As-Saraya Museum, Irbid, Jordan, for permitting the study and sampling of the glasses from Pella. I am indebted to SJB for hours of discussion about the glass and the intricacies of the contexts in which it was found, for reading chapters and for much congenial support and encouragement;

Dr Ralph-Bernhard Wartke, Deputy Director, Pergamon Museum, Staatliche Museen zu Berlin, for allowing me to study glasses from Assur and Babylon and for providing samples for analysis. Restraints of time and space have unfortunately prevented the inclusion of the results of these analyses in the present study, but they will be the subject of future publications as they provide important information on Iron Age glasses.

Dr Bernard Gratuze, of IRAMAT, Centre Ernest Babelon, C.N.R.S., Orléans, for most generously supplying me with his analytical data and reports for comparative glasses from France and thereby adding a valuable dimension to this work.

The many people who opened the collections of their institutions for me to study. The opportunity to learn about early ancient glasses by direct examination was invaluable:

Dr Ralph-Bernhard Wartke, Deputy Director, Pergamon Museum, Staatliche Museen zu Berlin, Ms Maude de Schauensee, formerly Keeper of the Near Eastern Section, the University of Pennsylvania Museum of Archaeology and Anthropology; Mr Raymond Tindel, Registrar and Senior Curator, Museum, Oriental Institute of Chicago; Dr Rachel Sparks and Mr Ian Carroll, Petrie Palestinian Collection, Institute of Archaeology, University College, London; Dr Rita Freed, Chair, Art in Ancient World Department, Boston Museum of Fine Arts; Professor Carl Lamberg-Karlovsky, Harvard University, Curator of Near Eastern Archaeology, the Peabody Museum, Dr Karin Sowada, Assistant Curator, Nicholson Museum, University of Sydney.

Dr Robert H. Brill, of the Corning Museum of Glass, for inspiration and early guidance, and for generously

furnishing the Corning standard reference glasses, B, C and D.

The people who have assisted with sample preparation and who have performed analyses of ancient glasses for this project (in addition to ICF):

Dr Alan Grieg and Dr Balz Kamber, formerly of ACQUIRE, for their inductively coupled plasma mass spectrometry analyses of the glasses examined in the present study. Their instruction and advice in geochemical interpretation of the resulting highly sensitive data was invaluable; Ms Alanna Simpson, University of Queensland, for electron probe microanalyses of the glasses from Nuzi; Mr Nigel Meeks, Department of Scientific Research, the British Museum, for assistance during sample preparation and scanning electron microscope analysis at the museum; Mr Adam Sikorski, Australian Key Centre for Microscopy and Microanalysis, University of Sydney, for assistance during sample preparation.

The many fine people who have been helpful in their stimulating discussions and encouragement, in particular: Dr Andrew Shortland, Dr Caroline Jackson, Dr Paul Nicholson, Mr Mark Wypyski, Dr Colleen Stapleton, Professor Julian Henderson, Professor Michael Baxter, Professor Mike Tite, Dr Julian Reade and Professor Janet Duncan Jones.

Professor Simon Ringer, Director of the Electron Microscope Unit (EMU), Australian Key Centre for Microscopy and Microanalysis, University of Sydney, for generously supporting me while employed at the EMU during my doctoral journey. In being a part of the EMU, I have found myself immersed in a stimulating environment of scientific research, filled with people whose interest and enthusiasm have inspired me.

Dr Melanie Fillios, Australian Research Council post-doctoral fellow, University of Sydney, for performing statistical testing of the Late Bronze Age glass data, and Mr Dennis Dwarthe, Senior Microscopist, the EMU, for checking the results and for assistance with use of the Sensi-Cam light microscopy system used to take light micrographs of glasses.

The efficient and helpful staff of the Fisher Library, and its branches, at the University of Sydney, who have

expedited my research. Ms Beth Hylén of the Rakow Library at the Corning Museum of Glass for her equally kind assistance.

The people who work at the University of Sydney excavations at Pella in Jordan, where this project began, who each encouraged and endured my last month of writing, which I undertook on site during the 2009 excavation season. It seemed poetic that this work should end where it began.

My caring and persevering family, friends and colleagues, some of whom have already made this journey and have guided me with unending patience:

Dr Catriona Bonfiglioli, Dr Paul Donnelly, Dr Tiffany Donnelly, Mrs Fiona Wotton, Mrs Joan Downton, Ms Liz Fenner, Mr David Bridges, Dr Bernadette McCall, Dr Michael Rodriguez, Dr Liz Carter, Dr Kate da Costa, Dr Kyle Ratinac, Mr Aneal Chandra, Dr Lloyd Weeks, Dr Cameron Petrie and by no means least, Dr John Tidmarsh, and Dr Karyn Wesselingh, who have been constantly supportive, reassuring and long-suffering. KW and Mr Philip Cullan have been invaluable technical advisors for computer-related frustrations. I owe the preservation of my sanity to them.

My father, Professor Emeritus Peter C. Reade, for reading my work and patiently correcting my many sins of scientific expression, for advising me, and for being there. I will always be grateful to him, to my mother, Erica, and to my step mother, Ene, for nurturing my dream of becoming an archaeologist, and for helping me to move to Sydney after finishing school in Adelaide, to the only University in Australia which offered a degree in archaeology. Now, many years on, I hope this dissertation goes some way to thanking them.

To Will and Chloe, always.

To all of these people I am deeply grateful for sharing their vast knowledge, insight and experience from which I have tried to learn, not just about ancient glass, but about life in general. I dedicate this study to them in appreciation of the immensity of all they have done for me.

Abbreviations

Chronology

BA	Bronze Age
c.	circa
C	century
IA	Iron Age
LBA	Late Bronze Age
MBA	Middle Bronze Age
MB/LB	Middle Bronze Age to Late Bronze Age transition
n.d.	no date

Technical Terms

Av.	average
b.d.	below detection limit
EPMA	electron probe microanalysis
Fig.	figure
HCHC	high copper-high cobalt
HFS	high field strength
HMHK	high magnesia, high potash
HREE	heavy rare earth elements
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
kV	kilo electron volt
LCLC	low copper-low cobalt
LMLK	low magnesia, low potash
LREE	light rare earth elements
MDL	minimum detection limit
mg	milligram
mL	millilitre
MUQ	mud from Queensland
nA	nano Amps (measure of current)
no.	number
O	opaque
ppb	parts per billion
ppm	parts per million
REE	rare earth elements
Ref.	reference
RSD	relative standard deviation
SBS	sedimentary background signal
SD	standard deviation
SEM	scanning electron microscope
SEM-EDS	scanning electron microscope with energy dispersive spectrometer
SRE	sediment-related elements
T	translucent
turq.	turquoise
UCC	upper continental crust
μm	micron
wt %	weight per cent

%	where % is used to indicate proportions of chemical compounds in the text, it has been calculated by weight
Z	atomic number
*	as in MgO* denotes reduced or base glass oxide normalised

Oxides

Al_2O_3	alumina
CaO	lime
CoO	cobalt oxide
CuO	copper oxide
FeO	iron oxide
Fe_2O_3	iron oxide
K_2O	potash
MgO	magnesia
MnO	manganese oxide (referred to in text as manganese)
Na_2O	soda
P_2O_5	phosphorus pentoxide (referred to in text as phosphorus)
PbO	lead oxide
Sb_2O_3	antimony oxide
SiO_2	silica
SO_2	sulphur dioxide
TiO_2	titania

Elements

(for elements in order of atomic number see Chapter 2)

Al	aluminium
As	arsenic
Ba	barium
Be	beryllium
Ca	calcium
Cd	cadmium
Ce	cerium
Co	cobalt
Cr	chromium
Cs	caesium
Cu	copper
Dy	dysprosium
Er	erbium
Eu	europium
Fe	iron
Ga	gallium
Gd	gadolinium
Hf	hafnium
Ho	holmium
K	potassium
La	lanthanum

Li	lithium	Sr	strontium
Lu	lutetium	Ta	tantalum
Mg	magnesium	Tb	terbium
Mo	molybdenum	Th	thorium
Nb	niobium	Ti	titanium
Nd	neodymium	Tl	thallium
Ni	nickel	Tm	thulium
Pb	lead	U	uranium
Pr	praseodymium	V	vanadium
Rb	rubidium	W	tungsten
Sb	antimony	Y	yttrium
Sc	scandium	Yb	ytterbium
Sm	samarium	Zn	zinc
Sn	tin	Zr	zirconium

Chapter 1

Introduction, Background and Aims

1.1 Introduction (Figure 1-1)

Until the mid-2nd millennium BC, the production of glass objects in the Near East appears to have been limited, with very few examples recovered from archaeological excavations. From the late 16th C BC, the volume of glass production increased markedly, the evidence for which is found in the beads, small mould-made pieces, core-formed vessels, inlays and ingots excavated at sites throughout the Near East and Egypt. The present study was designed to determine the compositions of a selection of the early Near Eastern ‘mass-produced’ glasses from the Late Bronze and Iron Ages, as a means of identifying differences and similarities in their compositions which occurred during and between each chronological period. This information has been used to define possible regional variations in composition, and to investigate the raw materials used in glass-making at this time.

The glasses analysed in the present study were excavated from the sites of Nuzi in Mesopotamia, from the neo-Assyrian capital of Nimrud (both in northern Iraq), and from Pella in the Levant (northern Jordan). The Nuzi glasses and many of the Pella glasses are dated between the 16th C to the 12th C BC, or the Late Bronze Age (LBA). The remainder of the Pella glasses and the Nimrud glasses are dated between the 11th C and the 8th C BC, or the Iron Age (IA).

Much of the early Near Eastern glass that has been studied to date, has been excavated from Mesopotamian sites, such as Nuzi, Nimrud, Assur and Tell Brak, and hence traditionally has been referred to as ‘Mesopotamian’, a term often used to distinguish glass found in the broader Near Eastern region from that unearthed in Egypt. Moreover, Near Eastern or Mesopotamian craftsmen are sometimes referred to as ‘Asiatic’. It is necessary here to clarify the terminology used in the present study. The Near Eastern region encompasses modern Syria, south-eastern Turkey, Lebanon, Israel, Jordan, Iraq (Mesopotamia) and Iran. The glasses included in this study were found in both Jordan and Iraq, and have been described as ‘Near Eastern’. This term is used in the present study to include all glasses from the Near Eastern region where the origins of glass remain obscure, because the production centres have not yet been located. The term ‘Mesopotamian’ is used when referring to the works of authors who have referred to glass specifically from the Mesopotamian region.

The early glasses from the LBA appear to be the product of an already complex pyrotechnological industry, the origins of which have been much debated. The products of this industry include glaze, faience and frit, besides glass. This study is concerned with the investigation of glass only.

Oppenheim (1973a: 262) contended that glass manufacturing was not a new invention in the LBA, as evidenced by the discovery of isolated glasses which preceded the *floruit* of glass-making in the mid-2nd millennium BC, the result of a change in glass-making technology that led to increased production and the broad distribution of glass. This technological advance is evident in the appearance of new production techniques, such as fusing, marvering, trailing and core-forming of vessels, and the creation of a wider range of colours than had previously been used (Moorey 1999: 193). General summaries of the nature of glass and the technology and techniques of ancient glass production, which are beyond the scope of this dissertation, have been published by Newton and Davison (1989: 1-17, 54-69), Stern and Schlick-Nolte (1994: 19-95) and Schlick-Nolte and Lierke (2002: 11-40), for example.

When studying the earliest glasses, the traditional archaeological approach of visual classification by physical type is limited by the narrow and simple range of shapes of objects, other than vessels. It is difficult to determine the origin of these objects, and hence the geographic extent of their manufacture and distribution. From physical studies alone, it is impossible to know the nature of the raw materials used to make ancient glasses (see for example Matoian 1999: 56). Chemical studies, or compositional ‘fingerprinting’, are developing as a result of the increased interest in the practical questions that they can help to answer. Compositional studies are providing more information because of the refined and sensitive analytical instrumentation now available, although the results obtained from such analyses can be constrained by the limited survival of glass during millennia of interment, the dependency on the rigour of excavation for the collection and recording of glass, and that much of the early glass is weathered.¹ When glass decays, or

¹ Indeed, it is possible that glass objects made in an emerging and probably experimental industry, prior to the mid-2nd millennium, have not survived due to compositional instability, although the survival of glazes from much earlier periods suggests that it was already known how to make stable glass. For the effects of weathering on glass and the problems regarding sampling, see for example

weathers, its composition is altered (Freestone 2001), but what remains of the original glass can often be sampled from a broken edge, and chemically analysed, thus providing valuable information about one of the first synthetic materials.

Until recently, the relatively undeveloped state of this kind of investigation has consisted of isolated studies of glass from several sites in the ancient Near East. The data from many of these analyses have not been systematically compared with the available data from other studies of glass compositions, and hence are not viewed in regional, chronological or technological contexts. Trace element data have largely been interpreted in very general terms, and 'beyond broad technological affiliations, meaningful compositional groupings have been difficult to establish' (Freestone 2006: 201).

Initially, it is possible to investigate glass-making groups by using the major elements which comprise the base glass compositions, determined with relative accuracy by most investigators of early glass. The data produced by different analysts may be compared, and indeed this is usually unavoidable in archaeological work because it is either impossible or undesirable to sample artefacts repeatedly (Freestone 2005: 5). While acknowledging the difficulties of sampling archaeological glasses, which has often meant the analysis of small numbers of samples of random selection, Shortland and Eremin (2006: 582) advocated the analyses of a large number of samples to reveal compositional patterns successfully, and to provide a cohesive data-set for comparative purposes for other researchers. The present study aimed to fulfil these criteria for the glasses analysed therein.

With the improvement in the availability and capability of chemical analytical techniques in recent decades, it is now possible to characterise the compositions of ancient glasses to ultra-trace element levels measured in parts per billion (ppb). The data produced by such analyses are used to refine the initial major element characterisations of the glasses, and to determine as far as is possible the raw materials used in their production. In turn, it might be possible to relate glasses to their primary production group or region, as has been done with 2nd millennium BC Egyptian glasses (Shortland *et al.* 2007) and with AD 1st millennium glasses (Freestone 2005: 1). This information enhances the interpretation of the earliest glass-making practices and the sourcing of raw materials. Glass is, by definition, an amorphous material, made from a variable combination of natural materials of variable composition, making the determination of its elemental composition a difficult task. The more detailed the chemical data available,

the more enlightening, but the more complex, this task becomes.

A model which has been developed in the form of a flow chart to illustrate the processes involved in the present study appears in Appendix I.

1.2 Historical Background of Early Glass

The earliest glass objects appear throughout the Near East in quantity as the products of an already complex pyrotechnology² in the mid-2nd millennium BC, with the date generally agreed to be c.1500 BC or slightly earlier (Lilyquist *et al.* 1993; Nicholson 1993; Shortland and Eremin 2006: 581). Before this time, vitreous technology centred on faience production and the glazing of stone, with rare exception, for example a piece of raw glass from Eridu (Barag 1985: no. 179) and other sporadic finds described by Moorey (1999: 190-191).

During the LBA, the large territorial states of Egypt and the kingdom of Mitanni interacted with one another (Kuhrt 1995: 283) and, located between them, especially in the Syro-Levantine region, was a set of smaller states that owed allegiance to their more powerful neighbours. Egypt at that time exercised northward territorial expansion. To the east lay Kassite Babylonia and to the north was Hittite Anatolia. When the Mitanni state declined in the mid-14th C BC, it was followed by the rising domination of Assyria. To the east of Assyria was the kingdom of Elam, while the city-states of Syria and Palestine persisted, but were dependent on the great powers around them (van de Mierop 2004: 121) (Figure 1-2).

The development and proliferation of glass-making occurred in the cosmopolitan cultural framework of the Hurrian dominated northern Syro-Levant and Mesopotamia, and the powerful Egyptian state and its vassals. In the mid-2nd millennium BC, these cultures were connected by trade routes which led north-south along the Levantine coast and the Jordan valley from Egypt to Syria, and east along the arcs of the Tigris and Euphrates Rivers which formed the Fertile Crescent (Moorey 1989; 1999: 5-6, 10; Van De Mierop 2004: 127-135).

At this time, Cyprus, the Aegean and the coastal regions of the eastern Mediterranean, including Egypt, were connected by regular maritime trade. The inland regions, such as Mesopotamia, were not directly involved but were connected to the coastal traders by inland trade routes. The quantity of goods that entered the Near East from the west increased

Turner (1963: 37).

² It is beyond the scope of the present study to discuss the origins of glass in earlier pyrotechnologies.

in the second half of the 2nd millennium BC to unprecedented levels, and included ceramics, copper, tin, ivory and other products in a complex exchange network, vividly recalled by LBA shipwrecks such as those of Cape Gelidonya and Ulu Burun (Bass *et al.* 1989; Knapp 1993; Akkermans and Schwarz 2003: 352; van de Mierop 2004: 117). Textual evidence and arts and crafts demonstrate the internationalism of this period and the movement and exchange not only of goods, but of ideas and of people (Akkermans and Schwarz 2003: 354). Cross-cultural contacts have an impact on the development of technology through trade, itinerant craftsmen, written records and native craftsmen being educated abroad, with the consequent spread of ideas, styles or the techniques of crafts (McGovern 1995: 30).

The end of the LBA, c.1200 BC, and the commencement of the IA belongs to a period which is termed a 'Dark Age' that affected the whole of the eastern Mediterranean region. From this time, written records were scarce and there has been much debate regarding the various events that are thought to have contributed to the collapse of the LBA civilisations. The large urban centres and political systems of the eastern Mediterranean world experienced a period of crisis and collapse which saw the abandonment of several cities including Ugarit on the Syrian coast, Alalakh in south-eastern Turkey and Tell Brak in northern Syria. The Hittite state to the north, and Mycenaean Greece and Cyprus to the west, were destroyed, while Egyptian imperial involvement in the Near East was curtailed. The Middle Assyrian empire in Syria, which had emerged after the defeat of Mitanni in the late 14th C BC, held out until its territories were finally reduced by the middle of the 11th C BC. The once flourishing maritime trade of the LBA ended with the widespread destruction and political instability of the region (McGovern 1987a: 271; Liverani 1987; Dever 1992: 18-19; Drews 1993; Akkermans and Schwarz 2003: 358-359).

McGovern (1987a: 267) argued that the LBA cosmopolitan city-state system was transformed into a much more insular society in the early IA, with few foreign contacts and a lower standard of living, in part due to the disruption of trade. Elements of early IA material culture superficially appear to be different to that of the LBA, but cultural and technological continuity was also evident in the uninterrupted use of the same cemeteries and settlement sites and in elements of material culture (McGovern 1987a: 267-269).

The economic decline of the 'Dark Age' is reflected in the apparent reduction in the production of glass at this time. There is an almost total absence of glass finds dating from the end of the 2nd and the beginning of the 1st millennia BC, until the 9th to 8th C BC when

glass vessels and other glass objects, such as inlays and beads,³ were being made again in the Near East (von Saldern 1965; 1970: 205; 2004: 5-67; Harden 1968: 49, 53; Barag 1970: 131; 1985: 51; Webb 1987: 145; Moorey 1999: 198-199). Harden (1968: 53) proposed that from the 9th C BC onwards, during the IA, there were probably two centres of glass vessel production, one on the Syrian coast and one in Mesopotamia. Both made core-formed vessels and, more rarely mosaic glass, and they developed casting and cold-cutting of glass, as found at Nimrud, for example.

At the end of the 10th C BC, the Assyrian kings began a series of successful campaigns against the peoples to the west, establishing the Neo-Assyrian empire (c.900-609 BC), which they maintained by continued expansion through annual military campaigns to raid and subjugate their neighbours (Akkermans and Schwarz 2003: 377). In the IA, trade developed into a more commercialised and geographically widespread venture, no longer exclusively controlled by elite powers. The use of camels, after their domestication in c.1000 BC, meant that goods could be transported over long distances through formidable desert, such as that between Mesopotamia and the Levant, complementing the traditional LBA trade routes along the rivers of these regions. At the same time, Phoenician inhabitants of the Levantine coast sailed further west than the LBA traders had, opening up new sources of raw materials in a far reaching trading network and establishing colonies in Cyprus, North Africa, Sicily, Sardinia and Spain (Akkermans and Schwarz 2003: 9-10, 360-361, 386).

By the end of the 8th C BC, the Assyrians had conquered lands as far as the Phoenician states of western Syria and the Lebanese coast, and Babylonia was reduced to subject status, making the Assyrian empire the largest political entity the Near East had ever seen (Akkermans and Schwarz 2003: 378-379).

Before the fall of the Neo-Assyrian empire in the late 7th C BC, the sites of Nimrud, in Mesopotamia, destroyed in the late 7th C BC, and Hasanlu, in Iran, destroyed in the 8th C BC, are known for the quantity and variety of glass finds, which are securely dated to this period of the resurgence of glass-making in the IA (Moorey 1999: 198). At Nimrud, vessels are predominantly monochrome (many are colourless) mould-made and cut glass bowls (von Saldern 1965), rather than the polychrome core-formed vessels of the preceding LBA, which is indicative of significant technological change.

³ Harden (1968: 49) assumed, without evidence, that beads and other small objects probably continued to be made through the 'Dark Age', especially in Syria.

This change can also be seen in the typological distinctions between the LBA core-formed vessels and those of the IA, which are smaller, and of poorer quality glass and workmanship, and which exhibit no direct links with the earlier LBA vessels (Moorey 1999: 200). Barag (1970: 135, 171-174) remarked on the limited distribution of core-formed vessels from the LBA by contrast with the diffusion of vessels to remote and very different regions in the IA. The LBA vessels have a smaller variety of shapes, which were frequently made with a blue base colour, whereas the IA vessels have a much wider range of shapes usually made with very dark colours, such as dark brown, green-black (often referred to as 'black'), and sometimes with blue, turquoise, brown, yellow, and rarely white.

Glass all but disappeared from Egypt between the 11th/10th C BC and the 7th/6th C BC, the time of the troubled Third Intermediate Period. A small number of glass samples have been found, dated from the 26th Dynasty, but glass remains rare until the 4th C BC (Moorey 1999: 200; Nicholson 1993: 61). The lack of evidence for IA glass-making from Egypt, has led to the suggestion of a Phoenician or Assyrian origin for the Nimrud mould-formed bowls (Moorey 1999: 199). Von Saldern (1970: 209) was undecided as to whether the origins of IA glass were Phoenician, Syrian or Assyrian, and Barag (1985: 52-55) later argued for manufacture by Phoenician craftsmen perhaps working in Assyrian court workshops. Barag's opinion was based on circumstantial evidence which links the glass from Nimrud with Phoenician production, including glass inlays attached to 'Phoenician' carved ivories, and similar glass inlays on a cut glass bowl (von Saldern 1970: nos 29-30), a proposition which has been supported by Orchard (1978) and Moorey (1999: 200). The Phoenicians have been recognised as the manufacturers and exporters of well-crafted metal vessels, jewellery, ivory furniture components and glass objects (Akkermans and Schwarz 2003: 387-388).

1.3 The Early Glass Industry

Many writers have commented that glass was made to imitate precious stones, primarily lapis lazuli, turquoise and later, rock crystal, amongst other stones (see for example Pliny in Eichholz 1962: 155-157, 185, 255; Oppenheim *et al.* 1970: 9-15; Moorey 1999: 77). The status of glass as a highly prized material in its own right is evident, not only from the predominance of glass in the archaeological record in temples, palaces and elite burials, but from the ancient texts, such as the Amarna Letters, which draw comparisons between stones and glass, and which list glass as a prized commodity exchanged between the elite. It could be said that glass, inspired by stones, came to compete with them in value, and surpass them in the variety of its colours and applications. The Assyrian glass-making

texts contain recipes for the production of glass, but are not technically explicit, and hence the technology and raw materials of ancient glass-making remain incompletely understood (Oppenheim *et al.* 1970: 22-68; Moran 1992; see also Nicholson 1993: 49; Nicholson and Henderson 2000: 195-196; Nicholson 2007: 2; Shortland 2007: 261-262).

Little is known about where glass was produced in the LBA and IA Near East. The trade in glass ingots, such as those found in the Ulu Burun shipwreck of the late 14th or early 13th C BC close to the coast of Turkey (Pulak 1988: 14; Bass 1986; Bass *et al.* 1989), indicates that glass-making and glass-working could be separate industries, and that the formation of glass into objects could be carried out in locations far from the raw glass production site. The discovery of glass ingots at LBA and IA sites such as Ugarit, Nuzi, Tell Brak and Nimrud suggests that glass was worked at these places, if not made there (Moorey 1999: 202-203). That the division between glass manufacture and object production was widespread in antiquity has been widely discussed (see for example Baxter *et al.* 1995; Freestone *et al.* 2000: 66-67; Gorin-Rosen 2000; Nenna *et al.* 2000; Matoian 2000a; 2000b; Rehren *et al.* 2001; Shortland 2007: 262-267).

Glass-making remains rare and, to date, are documented only in Egypt at Tell el-Amarna (Nicholson 1995a; 1995b; 1996; Shortland and Tite 1998; Shortland 2000; Nicholson 2007 for example), Malkata (Mass *et al.* 2002: 68; Nicholson 2007: 21) and at Qantir-Piramesses (Rehren and Pusch 1997; 1999; 2005; 2008; Rehren *et al.* 1998; Schoer and Rehren 2007). It is believed that glass was made in the Near East at this time, possibly in the Syro-Mesopotamian region in several production centres, but no definitive glass-making remains have been identified (Moorey 1999: 201-202). Although Pliny's account in his *Natural History* (Eichholz 1962: 151) of the origins of glass-making in the sands at the mouth of the Belus River in modern Israel is considered to be apocryphal⁴ (Wedepohl 1997: 247), other strands of circumstantial evidence point tantalisingly to the production, if not the origin, of glass-making being in the north Syrian or Mesopotamian regions. Such evidence includes the use of two key words in the textual references to glass; *mekku*, of West Semitic origin, found in texts from Anatolia, Syria and Nuzi in Mesopotamia, is synonymous with the word *ehlipakku* which is used in the Assyrian glass-making texts and is possibly of Hurrian origin. Both refer to 'raw glass' which the Egyptian king sought from the local rulers of Palestine, such as Tyre, recorded in the Amarna Letters of the 14th C BC. The Assyrian glass-making texts from the library of Ashurbanipal, of the 7th C BC, are

⁴ Turner (1956c: 277T-279T) summarised the ancient references to glass-making ingredients and the connection of the Belus River sands with glass-making along the Syrian coast for many centuries.

believed to have had their origins earlier in the 12th C BC (Oppenheim 1970; 1973a; Moorey 1999: 195).

While the regular production of glass in quantity, and particularly of vessels, is considered to have occurred in northern Syria or Mesopotamia because of the geographic distribution of excavated glass artefacts at sites such as Nuzi, Tel al-Fakhar, Tel al-Rimah, Tel Brak, Assur and Nineveh, all sites which were under the domination or influence of the Hurrians (Petrie 1926: 230; Beck 1934: 8, 19; Harden 1956: 319; 1968: 46-47; Barag 1970: 184; Grose 1989: 45-48; Tite *et al.* 2002: 589), glass manufacturing in Egypt is now generally believed to have begun shortly afterwards (Oppenheim 1973a: 263; and see Nicholson 1995a: 11-19, Nicholson *et al.* 1997: 143, 147; Jackson *et al.* 1998: 11-12; Nicholson and Jackson 2000: 11-21; Shortland 2000c; Shortland and Eremin 2006: 581 for example).

Bryan (2000: 247) proposed, from her study of Egyptian tombs from the time of Thutmose III and Amenhotep II, that 'the prestige of things Syrian began to soar'. Not least amongst these luxury items was glass, for example the glass vessels made to imitate marble, found in the tomb of Kenamun (TT162). That the military aspect of the Egyptian encounters with the Mitanni was directly responsible for the introduction of glass to Egypt is strongly suggested by Bryan (2000: 247), who believed that the production of glass at this time could have developed in Mitanni centres, such as Tell Brak and Tell Rimah.

Egyptian representations of Syrian workmen being brought to Egypt, carrying vases of metal or glass they had made, had also suggested to Petrie (1926: 230) that glass originated in Syria or Mesopotamia, although glass from this time is much better preserved in Egyptian soils than in those of the regions to the north, and provides a larger corpus for study (Harden 1968: 48; Moorey 1985: x; Newton and Davison 1989: 19). The Syrian origins of glass were discussed by Oppenheim (Oppenheim *et al.* 1970: 57, 84-6; 1973a: 9-11; 1973b: 261) Moorey (1985: 197, 201-2) and McGovern *et al.* (1991: 401).

Nicholson (1993: 45, 47) and Nicholson and Jackson (2000: 11-12), through their work at the pivotal Egyptian glass production site of Amarna, acknowledged that the Mesopotamian region was the 'cradle' of glass-making, and that the first glass to be found in Egypt was either imported from Mesopotamia or was made in Egypt by Mesopotamian craftsmen.⁵ They reviewed current opinion which held that Egyptians of the early New Kingdom could not make glass (for example Newton 1980: 176; Newton and Davison 1989: 62, 107), whereas

Lilyquist *et al.* (1993: 43) determined that there was evidence for the importation of Near Eastern glasses and that 'Asiatic' craftsmen were present and making glass in Egypt, as Oppenheim had suggested earlier from philological evidence (1973a: 263). That early glass from the reign of Thutmose III was imported into Egypt from the Near East as tribute from the chiefs of Syria was discussed by Shortland (2000c) with reference to descriptions of glass in two Theban tombs of this date. Shortland (2001) continued his examination of the earliest glasses found in Egypt concluding that while some of these glasses were likely to be imported from the Near East, the cobalt blue glass found from the time of the reign of Thutmose III must have been a local Egyptian product.

Nicholson and Jackson (1998) showed, by making glass in a replicated furnace, that the excavated furnaces at Amarna could have been used for making glass, a conclusion that was supported by the work on Amarna glasses by Shortland and Tite (2000). Rehren and Pusch (2005: 1757) and Schoer and Rehren (2007: 173) have showed convincingly that the finds from Qantir-Piramesses, including cylindrical vessels filled with partly fused glasses, are evidence that glass was made at this location in Egypt. In his detailed archaeological analysis of the origins of glass found in Egypt, Nicholson (2007: 1-4, 8) highlighted the important relationship of Mitanni with Egypt when he observed that the Amarna letters recorded Mitanni as a source of glass which was exploited into the Amarna period, but noted this did not mean that the New Kingdom Egyptians could not make glass themselves (Nicholson 2007: 4). The Egyptian origin of the glass ingots from the Ulu Burun shipwreck was established by Nicholson *et al.* (1997) and, considered with the remains from Amarna and Qantir-Piramesses, provided convincing evidence for local Egyptian glass-making (Jackson 2005a: 1751).

The organisation of LBA glass workshops is thought to have been centred in palaces and temples of major cities, where much of the glass and glass-working remains have been found, although Moorey (1999: 197, 202) did not discount the possibility of small-scale production outside the sphere of palace and temple workshops. McGovern *et al.* (1991: 401) thought that the different chemical compositions of the glasses from sites such as Tell al-Rimah, Nuzi, Nippur and from the Baq'ah Valley demonstrated that glasses were largely produced by well-developed, local industries, while their similarities indicated that they shared a common technological tradition.

Sparks (2001: 96, 109) explored the practice of locating workshops which produced valuable goods under palace control, with reference to a luxury obsidian workshop at Tell Atchana, commenting that 'a high degree of organisation and wealth would have been

⁵ See section 1.1 for explanation of the usage of the terms 'Mesopotamian' and 'Near Eastern' in this study.

essential in maintaining a craft requiring imported luxury raw materials'. Glass-making from raw materials and the importation and subsequent working of glass ingots might be considered in the same light. Glass ingots and many pieces of cullet were found within the LBA palace at Tell Brak in northern Syria which Oates *et al.* (1997: 81, 85-86) interpreted as evidence for glass manufacture, or at least glass-working, from as early as the 15th C BC. There was no evidence of a workshop at LBA Ugarit (Ras Shamra) on the Syrian coast, but it has been hypothesised by Matoian (1999: 56) that vitreous materials were made there because of the 'exceptional and original' objects recovered, amongst the small chunks of glass, Egyptian blue and cobalt, and hundreds of vitreous objects (Matoian 2000b: 41-42).

Evidence from two known glass-making sites in Egypt provide insight into the organisation of the glass industry in that region during the 2nd millennium BC. Rehren *et al.* (1998) described the industrial complex of Qantir-Piramesses in the Egyptian delta where evidence suggested that bronze casting and vitreous materials production were integrated in a highly specialised organisation of shared pyrotechnologies and skills. The interdependence of glass, faience, frit and pottery production at Amarna was described by Shortland and Tite (1998) who examined and chemically analysed the material evidence.

The study of the organisation of glass- and faience-making at Amarna was pursued by Shortland *et al.* (2001) who believed that although faience and glass were made using the same facilities, the raw materials used in their production were different. Glass was linked to royalty, partly by the connection evident in textual evidence, and also, the authors suggested, by the possible temple or state control of special colourants like cobalt.

Faience appeared to have a lower socio-economic distribution because it was a common material found in many houses (Shortland *et al.* 2001: 151, 154-155). Shortland (2007) concluded from philological and textual evidence and from the remains of glass-working premises at Amarna, that the glass-workers there were of lowly status in a hierarchy of possibly three ranks that encompassed a glass-making and glass-working industry that was closely controlled by the royal court.

Ritual and divination techniques were applied to the more highly regarded glass production process (Oppenheim 1970: 32-33, 44-47), which was probably carried out within the temple grounds. Robson (2001: 54) made the observation that the 'boundaries between science and religion, medicine and magic were always blurred in the ancient Near East' and hence it is not surprising that the production of glass was a combination of practical and ritual procedures.

Shortland (2008: 67) made the significant comment that the ritual nature of glass-making had the 'effect of stifling technological choice and prohibiting experimentation and innovation'.

Robson (2001: 51-52) argued that different colours of glass were believed to have magical properties including curative powers. That the magical and medical fields lay within the sphere of priests explains why the recipes for making artificial stones were included in the corpus of literature to which the glass texts belong. It is believed that these recipes were handed down from the mid-2nd millennium BC as part of a codified tradition that might have been outdated by the 1st millennium BC when, as Robson believed, it was no longer fashionable to make coloured glass (Robson 2001: 53). While different colour preferences are evident in IA glasses, there is no reason to conclude that they did not continue to imitate, and indeed even rival, stones. Dark and turquoise blues, red and purple, known from the LBA, are found also at IA sites, such as Nimrud, and the emergence of larger numbers of colourless glasses might be the result of an advance in technology that enabled the imitation of rock crystal.

Rehren *et al.* (2001), in view of material evidence from Qantir and other sites, proposed that the Egyptian glass industry consisted of primary and secondary workshops, where glass-making and glass-working were carried out separately, a theory not incompatible with that proposed by Shortland (2007). Rehren and Pusch (1997; 2007: 231-233) and Rehren (2000b; 2005), from their research at Qantir-Piramesses, proposed that in the LBA different workshops specialised in the production of particular colours, for example red glass was made at Qantir and cobalt blue glass at Amarna (Jackson and Nicholson 2007: 114-115). The manufacture of these colours required special ingredients or specialist knowledge, but it has not yet been possible to attribute other colours, such as yellow and white, to particular workshops due to the lack of evidence regarding primary production sites. Petrie (1926: 230), in noting that early glass was coloured in imitation of precious stones, found it interesting that the earliest glasses were in fact coloured rather than left in their natural 'colourless' state, because the ability to colour glass required a high degree of specialisation. Nicholson and Henderson (2000: 197, 214) commented that it was easier to colour than to decolour glass and this might more readily explain the lack of truly colourless glass at this time, but does not explain the lack of naturally uncoloured glass, which would have been easier to produce than either intentionally coloured or decoloured glass.

Rehren (2000b: 22) suggested that copper blue glass could have been produced at a number of different

manufacturing locations in LBA Egypt and the Near East because copper was readily available. Copper concentrations in blue glasses have a wider variability of composition, which suggests that the glasses were the products of different workshops. Glass working, on the other hand, encompassed the entire range of colours, which could have been traded from their places of specialist manufacture.

The compositional homogeneity of LBA Egyptian plant ash glasses⁶ for approximately 500 years was seen by Rehren (2008: 1346) as a possible result of a closely controlled raw material supply and workshop practice, as could be expected from an elite material under strict control, in the same way that LBA Near Eastern glass production was described by Robson (2001) and Shortland (2008). Glass working remains in the royal palace at Nimrud suggested that royal control continued to be exerted over this industry in the IA (von Saldern 1965: 241.2; Moorey 1999: 202-203).

1.4 Object Studies

The typological studies of LBA and IA Near Eastern glasses, in which vessels and moulded objects have been assembled and classified with regard to shape, decoration, chronology and origin, have been central to our understanding of early glass-making in this region, providing the archaeological context for subsequent research. This information was established largely by the works of Fossing (1940), Harden (1968),⁷ Barag (1962; 1970; 1985) and von Saldern (1965; 1966a; 1966b; 1970). Fossing (1940) collected the limited material available at the time, although his dating of the early glass industry in Mesopotamia has now been extended earlier into the LBA. Von Saldern traced the history of Mesopotamian cut glass vessels of the 8th C BC onwards from the site of Gordion in central Turkey (1959), and mosaic glass from Hasanlu and Marlik in Iran, Tell al-Rimah (1966) and from Nimrud (1965; 1966) in Iraq.

Barag (1970: 131) surveyed the archaeological evidence for the production of core-formed glass vessels made in Mesopotamia from the mid-2nd millennium to the mid-1st millennium BC, for which there is no textual evidence. He identified two distinct groups, corresponding to the LBA, 15th-13th C BC, and the IA after the 'Dark Age', 8th-6th C BC. From his examination of the archaeological evidence from Palestine and Syria, Barag (1970: 185) was in no doubt that contemporary glass vessels from Mesopotamia had a different, probably local, origin. He surveyed the connections between the Aegean, the Syro-Levantine region and Mesopotamia, considering

nude female pendants, star and plain disk pendants, and spacer beads, such as those found at Nuzi. Barag concluded that they were produced in Mesopotamia, but noted that they also could have been made in the Syro-Levantine region (Barag 1970: 188-193). The work of von Saldern (1970: 203-212) complemented that of Barag with a chronological study of Near Eastern glass, other than core-formed glass, from 1500 to 600 BC. He observed the move from opacity to translucency in IA glass, and that the bowl, a shape found at Nimrud, became the most popular form at this time. After Nimrud fell in 612 BC, the manufacture of transparent luxury glass continued in the same region and further west into Achaemenid and Hellenistic times.

Catalogues of glasses from the Near East, Egypt and the Mediterranean from the mid-2nd millennium BC to the early Roman period were compiled by Grose (1989) and Stern and Schlick-Nolte (1994). Grose's study focussed on the typology and chronology of objects, and Stern and Schlick-Nolte added a summary of manufacturing techniques.⁸ The addition of chemical 'typologies' to the physical object data continues to add immensely to the current state of knowledge of LBA and IA glass production and is summarised in the following sections.

1.5 Early Chemical Investigations

Early chemical studies of BA glasses from the Near East, from the early sporadic finds prior to the mid-2nd millennium BC through the increased production during the LBA, are summarised well by Moorey who commented that, although the compositional database was slowly increasing, there remained a remarkable lack of progress in the chemical study of the earliest Near Eastern glass (1999: 190-198, 206-210; see also Henderson 2000: 48-51).

Although only small numbers of glasses were analysed in the early compositional studies, they were important, nevertheless, for providing the basis of current knowledge and the foundations for subsequent research. The work of Turner (1930; 1954; 1955; 1956a-d; 1963), Turner and Rooksby (1959; 1961; 1963), Sayre (1963; 1964; 1965), Sayre and Smith (1961; 1967; 1974), Smith (1963) and Brill (for example 1999a; 1999b, amongst others) made important contributions to our understanding of the compositions of early glasses. Their work is summarised briefly in the following sections and recent research is reviewed to provide the background, context and impetus for the present study.

For ancient Egyptian glass technology, works by scholars such as Lucas (Lucas and Harris 1989: 179-194), and Nicholson and Henderson (2000: 195-226) have

⁶ Early base glass compositions are reviewed in sections 1.5 to 1.9.

⁷ Harden (1984) published an interesting review of previous, and sometimes forgotten, early studies of glass which fall outside the focus of the current work.

⁸ Earlier, Stern (1993) published a brief description of glass-working techniques before the advent of glass blowing.

made their own valuable contributions to this field, combining chemistry and history in a more holistic approach. Henderson's textbook on the science and archaeology of inorganic materials is an informative, and general work, in which the glass technology of several periods and regions is summarised (2000: 24-109).

Turner (1930), in his study of ancient glass, reported that soda acted as a flux to lower the melting temperature of silica, and lime served as a stabiliser. Ash of the plant *Salicornia* was thought to have been used to provide the soda for the flux (Turner 1956a). The composition and use of plant ashes in glass-making have been studied intensively in recent years in an attempt to understand which plants were used and how they were processed (section 1.8).

Turner's (1956c: 282T-291T) findings provided the essential characterisation of ancient glasses which are now termed 'soda-lime-silica' glasses after their main components, which were silica from quartz or sand, soda as the dominant alkali from plant ash, or mineral soda, and lime which was introduced as part of the plant ash or sand component. To this base glass was added colourant, opacifying or decolourant agents. The remaining components, such as potash, magnesia, alumina and iron oxide, were included in the glasses by association with the main ingredients. Each ingredient could be complex in character and variable in composition (Turner 1956c: 296T), which adds to the difficulty of identifying raw materials from glass compositions. These early chemical descriptions of ancient glasses were important in forming the basis of our understanding of ancient glass compositions and the raw materials used to make them, and have been the inspiration for subsequent studies.

Sayre and Smith (1961) looked at a similarly wide chronological and geographical range of glasses and, building on Turner's work, identified five main categories of glass composition. The group designated as glass of the 2nd millennium BC (15th C to c.7th C BC) from Egypt, Mesopotamia, Mycenae and Elam, was found to be of the soda-lime-silica type with a high magnesia content. The other four categories are comprised of glasses of later dates than are relevant to the present study, but with compositions that served to distinguish them from the earliest glasses.

Smith (1963) refined the classification of the five categories of ancient glass by identifying high- and low-magnesia glasses, of which the 2nd millennium glasses were classed as high-magnesia while the later 'antimony-rich' and 'Roman' groups were of low-magnesia content. Potash content was found to follow the same pattern as magnesia, but with greater overlap

of concentration between the high- and low-magnesia groups. Sayre and Smith (1974: 56, 58) observed that there were two groups of soda-lime-silica glasses: high-magnesia, high-potash (HMHK) and low-magnesia, low-potash (LMLK), which depended on the use of different types of alkali. Brill (1999a: 277) has more recently defined HMHK glasses as having contents of these oxides in excess of approximately 1.5%, whereas LMLK, or natron-type, glasses have contents of these oxides between 0.5% to 1.5%.

The HMHK glasses were known from the 2nd millennium BC Near East until approximately the mid-1st millennium BC when HMHK glass from sites west of the Euphrates all but disappeared. The discovery of a few high magnesium glasses from the last half of the 1st millennium BC suggested that there was some continuation of the high magnesium tradition at the relatively eastern sites of Nippur and Persepolis. The HMHK technology was reintroduced widely in Islamic times (Sayre 1964: 9-11; 1965: 151; Sayre and Smith 1967: 283). The results of Brill's (1999b: 43-44, 46-47) analyses of glasses from Nimrud and Hasanlu show that the high magnesia tradition also continued at these eastern sites.

The LMLK glasses, on the other hand, were believed to have appeared from the mid-1st millennium BC when the HMHK tradition declined (Sayre and Smith 1974: 58). This proposition was not challenged until the discovery of the 10th C BC LMLK glasses from the burial of Nesikhons in Egypt (Schlick-Nolte and Werthmann 2003; section 1.5), and the analysis by Brill (1999b: 46-47) of LMLK (non-cobalt) glasses from Nimrud, the results of which were compiled in a publication without interpretation, show that these glasses pre-dated the appearance of other documented LMLK glass by up to half a millennium.

The translation of the neo-Assyrian glass-making texts published by Oppenheim, with the accompanying chemical interpretation by Brill, and the surveys of core-formed and other vessels from the mid 2nd millennium BC to the mid 1st millennium BC by Barag and von Saldern (section 1.4), made a highly significant contribution to our knowledge of the technological history of Mesopotamian glasses (Oppenheim *et al.* 1970). Brill (1970a) interpreted the chemical and technical information of the texts, which were of a literary nature rather than explicit instructions for glass-makers, and he and Oppenheim identified quartz pebbles and plant ash as the chief ingredients, although many other ancient terms remain unclear (Brill 1970a: 109-110). To show that the recipes in the texts were indeed for glass, Brill sourced appropriate raw materials and replicated the production of ancient glass, and found it to be of a high quality. Brill (1970a:

113) commented that different ashes and silica sources could be used to achieve similar results.

After the early definitive studies of glass compositions and their general observations on the nature of raw materials, scholars have often pursued research into specific and increasingly complex aspects of glass-making and raw materials studies. The availability of sensitive analytical techniques on which this kind of research relies has already been mentioned, and it is these techniques that allow researchers to undertake detailed compositional studies of larger numbers of ancient glasses from a range of sites. The data obtained can be used to investigate a range of archaeological and technological questions about ancient glass production. Research concerning the various components of ancient glass and compositional studies of glass from the Near East and Egypt are considered in the following sections.

1.6 Silica

The major ingredient of glass is silica in the range of approximately 60% to 70%, sourced primarily from quartz or sand. In early studies, Turner (1956c: 279T, 281T) analysed the compositions of sands and showed how their alumina and iron contents, components of clay and other minerals which occur as impurities in sands and in the refractory containers used in melting glass (Matson 1951: 84; Henderson 1985a: 270-271; Lucas and Harris 1989: 481), would have contributed to the glass compositions. More recently, Rehren and Pusch (2007: 223-225) have experimented with grinding stones from Qantir to show how they contributed contaminating elements, such as aluminium, potassium, calcium, titanium, strontium, zirconium, barium and transition elements, to the silica when quartz pebbles were being crushed.

The composition of possible glass-making sands and quartz pebbles from the Near East, Egypt and southern Turkey have since been analysed by Bezborodov (1975: 57-60), Brill (1999b: 474-479) and Degryse *et al.* (2005: Tables 5 and 6, 294-295) amongst others, identifying the range of contaminants that would have been incorporated into glasses made from them, for example alumina, iron, lime, soda and potash. Tite *et al.* (1998: 118) proposed that iron oxide content in glass of less than 0.6% indicates the use of quartz as the source of silica, which introduces very low concentrations of impurities to the final glass. Nicholson and Henderson (2000: 197) noted that a sand source of silica must have been used to make Egyptian glasses because of their relatively high alumina and iron oxide contents (see also Shortland and Eremin 2006: 589).

Freestone (2006: 205-206) listed potential sources of silica as quarried siliceous minerals and rocks, such as vein quartz, chert and quartzite, as well as pebbles of

these materials and coastal or inland sands. Freestone investigated the nature of the coastal sands of Israel, including those from the Bay of Haifa into which the Belus River flows. Emery and Neev (1960) noted that beach sands of Israel are derived mainly from the Nile River with mineral contributions from other sources. Their research showed that sands along the coast of Israel have variable composition, including that of lime derived from sea shells and the remains of other forms of marine life. The variable composition of these coastal sands is reflected in the glasses made from them as demonstrated by Freestone *et al.* (2002: 265) in their study of Byzantine glass from Maroni Petrera in Cyprus.

If lime-bearing plant ash was used to flux glass made from sand, that sand would have to have a low lime content to avoid the incomplete melting or devitrification of the resulting glass that is caused by an excessive concentration of lime (Freestone and Gorin-Rosen 1999; section 1.7). For this problem to have been avoided, HMK or plant ash glasses are assumed to have been made with pure quartz pebbles or relatively pure sand, and LMLK glasses with a lime-bearing sand and mineral soda mix. When Egyptian mineral soda was first used to make glasses in the 10th C BC, for example, silica was derived from quartz or low-lime sand in the HMK tradition. The resulting glasses, such as those belonging to Nesikhons (Schlick-Nolte and Werthmann 2003), were chemically unstable due to low lime levels, showing that the selection of a glass-making sand with sufficient lime would have been critical for the preservation of mineral soda fluxed glass. It is inevitable that other early unstable LMLK glasses would not have survived without favourable burial conditions, explaining the limited evidence of this important technological change (Freestone 2006: 208).

Nicholson and Jackson (2000: 20; Jackson and Nicholson 2007: 98) found that they could make a good quality glass of similar composition to those analysed from New Kingdom Egyptian contexts using a soda-rich plant ash and sand, although it must be assumed that the total lime content of the sand and ash mix was low enough to achieve an enduring glass that did not vitrify (see also Nicholson and Jackson 1998; Freestone and Gorin-Rosen 1999). Shortland and Eremin (2006: 589) argued that the apparent wide availability of reasonably pure sands in Egypt meant that sand could possibly have been used to make plant ash fluxed glass. Rehren and Pusch (2008: 30) have more recently confirmed that crushed quartz was the source of silica in glasses made at Qantir Piramesses, thus it would appear that either a low lime, or non-calcareous, sand or quartz could be used to make plant ash fluxed glasses.

Similar work has not been done for glasses from the Near East for this period, although the research of

Freestone and co-workers (Freestone and Gorin-Rosen 1999; Freestone *et al.* 2000) on the compositions of Byzantine and Early Islamic glasses from Israel showed that coastal sands near the mouth of the Belus River were too rich in lime to have been combined with plant ash to produce enduring glass (section 1.7).

1.7 Lime

Lime acted as a stabiliser to reduce weathering of the silica-soda glass network (Henderson 1985a: 277). While elements such as aluminium or iron also had preservative qualities at elevated levels, lime was a key component of ancient glasses, hence their designation as 'soda-lime-silica'.

The question as to whether lime was deliberately added to ancient glasses has been much debated. According to the two-component model of glass-making, silica and a soda-rich flux were the chief ingredients, with lime entering the glass with either or both of them (section 1.5).

Pliny (Eichholz 1962: 153) made an enigmatic reference to the addition of shells to the glass batch, presumably as a source of lime, but the otherwise scant mention of lime in ancient texts, and no mention of lime or magnesia in later texts until the 18th C AD, led Turner (1956a; 1956b: 175T-176T) to conclude that until this time glass-makers did not know that their glasses contained these substances, and yet lime has been an important and substantial component of most of the glasses that have survived from early times, acting as a stabiliser for the soda-silica network.⁹ The anomaly between what has been written in past times and the actual composition of the ancient glasses has led to much discussion as to how the glass-makers could not know about lime, and in what form it must have been added to the glasses.

Henderson (1985a: 272) cited the greater durability of prehistoric soda-lime-silica glasses compared with that of medieval potash glasses as being an example of a long-term technical regression in glass-making. It could be extrapolated from this that the medieval texts concerning glass-making are not necessarily reflective of the knowledge of ancient glass-makers, and could not be an accurate indication of their knowledge of the use of lime. Smedley *et al.* (1998: 149) suggested that if the ratio of alkalis was monitored by taste, this knowledge in time would be taken for granted, and not recorded. Shortland (2007: 263), in considering

the lowly depictions of medieval glass craftsmen in contemporary and later manuscripts, questioned the validity of using what we know of medieval glass craftsmen to represent ancient glass-workers, and concluded from archaeological and philological/textual evidence that 'the more spiritually complex and challenging world of the second millennium BC' could not be represented by more recent glass production models (Shortland 2007: 271-272) (section 1.3).

Turner (1956c) noted the high lime content of sands from Tell el-Amarna and Karnak, which are adjacent to long limestone bluffs, and from Gizeh and the mouth of the Belus River. Sayre (1965: 146) agreed with Turner's argument that lime was likely to have been present in the sand. Sayre and Smith (1967: 280) found a correlation between magnesia and potash, and other alkali metals, and a lack of correlation between lime and magnesia, which seemed to discount the idea that dolomitic limestone was used to make ancient glasses, as had been proposed by Matson (1951: 84). To enable the addition of measured quantities of lime to the glass batch, Nicholson and Henderson (2000: 216) proposed that shell fragments were separated from sand and used as an individual lime source, although Brill (1970: 109) had suggested that the proportion of shell in a sand would be constant. Deliberate incorporation of lime or limestone as a separate component in Egyptian glasses was supported by Tite *et al.* (1998: 118) and Shortland and Eremin (2006: 590-591), while Henderson (1985a: 288) argued against the addition of limestone and Rehren (2008: 1346) also disagreed, maintaining that neither calcareous sand nor lime were deliberately added by the glass-makers. Cosyns and Hurt (2007: 6) were also of the opinion that lime was unintentionally added to the ancient glass batch as a component of sand or plant ash.

Rehren and Pusch (2007: 231-233), through experimental work on the significance of the melting process and melting temperature on the alkali content of ancient glass, concluded that the lime parting layer applied to the inside of the melting crucibles added lime to the glass batch as the furnace temperature increased (see also Rehren and Pusch 2005: 1756; Smirniou and Rehren 2011). It is not known whether the glass-makers realised that when they used lime in this way that it was also a key ingredient of the glass. Rehren and Pusch (2007) did not consider whether a lime-rich wood ash could have been used as fuel in the furnace and thereby become incorporated in the glass batch. Contamination of the glass batch by fuel ash was suggested by Jackson *et al.* (2003: 451) when explaining the composition of Roman glasses from Coppergate, York. Shugar and Rehren (2002: 147) proposed that the melting temperature of the glass batch directly controlled the lime content of the glass melt, but this must be dependent on the quantity of lime added to the batch before firing.

⁹ If glasses were made with insufficient lime, they might not have survived unless under extraordinary circumstances, such as the low-lime glasses found in the protective environment of the tomb of Nesikhons in Egypt (Schlick-Nolte and Werthmann 2003), section 1.5. McGovern (1995: 30) wrote, 'Archaeological data represent a very small, highly selective fraction of the original technology'.

When investigating Byzantine and Early Islamic glasses from Israel, Freestone *et al.* (2000: 70) found that a mixture of sand and natron, or of quartz and plant ash must have been selected by the glass-makers to produce glasses with similar ratios of silica: lime: soda. If lime-rich sand were mixed with plant ash, the resulting lime content would be too high causing the incomplete melting or devitrification (section 1.6), as was observed in the Bet She'arim slab from Israel of the 9th C AD, which contained approximately 16% lime (Brill and Wosinski 1965; Brill 1967: 92; Freestone and Gorin-Rosen 1999; and see also Matson 1951: 83). Brill (1988) demonstrated that the composition of the glasses from the Late Roman site of Jalame in Israel were consistent with manufacture from natron and beach sand from the mouth of the Belus River. Lime, in this instance, was introduced as shell occurring naturally in the sand. When Freestone (2006) examined Near Eastern glass production in Late Antiquity and the early Islamic period, he concluded that lime was rarely deliberately added to glasses of the 1st millennium AD (2006: 207), agreeing with Brill's similar observation that early Indian glasses were made from a two-component batch (1987: 7-8). Brill, however, commented that if a third basic ingredient became necessary as a stabiliser because the first two were too pure, then the third ingredient must have been intended to introduce lime, implying that these glass-makers had knowledge of the role of lime in glass-making.

The question of whether lime was added deliberately by the ancient glass-makers has not been resolved, although the weight of evidence suggests that lime was usually added either as part of the plant ash flux, or in a natural combination with silica sand. It is probable, however, that the glass-makers learnt from experimentation which combinations of particular raw materials produced an enduring glass. Henderson (1985a: 286) commented that the glass artisans must have understood their materials because they were able to achieve close control of the amount of colourant and presumably of the kiln conditions. It might be said, however, that cause and effect in colouring is readily observed, while presence or absence of lime is not visually identified. Research and argument continue.

1.8 Plant Ash

The role of plant ash in glass-making is to provide the alkali, particularly soda, as a flux to reduce the melting temperature of the silica component from 1710° Celsius (Henderson 1985a: 270-271). It is present typically between approximately 13% to 20% in early glasses. The continuing study of plant ash compositions has provided an understanding of the complex nature of this raw material, and how its composition might be related to the final glass it was used to make, although many questions remain to be answered.

In his commentary on the chemical aspects of the ancient Assyrian glass texts, Brill (1970a: 110) noted that the ashes of the 'Naga plant' could have been of the *Salsola* or *Salicornia* genera, as suggested previously by Turner, who recorded that plants grown near the sea would have had a relatively high soda content, desirable for glass-making, and that plant ashes contain many other constituents besides soda and potash (Turner 1956a: 42T; 1956c: 282T-291T).

Turner's (1956c: 282T-291T) basic analyses of 'Keli'¹⁰ ash from Syria, amongst other ashes, showed the great variability in the relative proportions of the constituents of ashes from different plants, and from the same plants depending on the locality in which they were grown. The variability of ash composition was confirmed by Brill's (1970a: 110, 124) analyses of Near Eastern and Mediterranean saline coastal and arid region plant ashes, and by Bezborodov's (1975: Table 5) analyses of different parts of the same plants which exhibited compositional variation. Brill (1970a: 110) commented that the soda to potash ratio in ancient glass of approximately 10:1 was an important indicator of the source of the alkali, as did Matson (1951: 84) and Turner (1956c: 282T-291T) before him.

The study of plant ashes as raw materials was advanced by Sanderson and Hunter (1981: 27-30) when they too examined the compositional variability of plant ashes (seaweed and wood ash) and of glasses made with plant ashes, and noted that there must have been many combinations of natural materials which resulted in the observed compositions of ancient glasses. Sanderson and Hunter were concerned that the conclusions of previous studies had been of a comparatively general nature and, like Smith before them (1963), urged further quantitative analysis of raw materials. The work of Smedley *et al.* (1998) on the glass-making practices recorded by Theophilus, highlighted again the variability of plant ash composition and that all of the oxides found in the ash would not necessarily be incorporated into the final glass. The variability of ash composition was reiterated by Canti (2003: 347) who added that soil adhering to the plants would affect the mineral content of the ash.

Brill (1970a: 110) noted that the way the ash was burned was also responsible for causing variation in its composition, a point made by Smedley *et al.* (1998: 152) who found that not all of the oxides present in wood ashes would be incorporated in the final glass because of decomposition or reaction during heating. Although wood ash compositions are high in potash¹¹ and hence

¹⁰ The word 'Keli' probably derives from the Arabic *al-qali* meaning plant ash (Biek and Bayley 1979: 6).

¹¹ The high-lime, high-potash nature of wood ash, used to make European glasses, is discussed by Henderson (1988) and Wedepohl

distinct from the high soda ashes used to make ancient Near Eastern glasses, the results of their study are worth considering, because they highlight issues which could apply to the study of other plant ashes. In view of this, it is interesting to note that in their study of wood ash, Misra *et al.* (1993) found that the content of potash and soda decreased as a function of temperature during ashing, while the concentration of lime was assumed to remain constant. This might give an indication of the effects that ashing could have on the original elemental content of the plants, and the complexities that this might impose on the interpretation of the relationship between the original composition of the plants and the final composition of glasses made from the plant ashes.

The proposition that alkali earth oxide concentrations in LBA plant ash glasses were controlled largely by the melting temperatures and the melting behaviour of the system was put forward by Tanimoto and Rehren (2008: 2567) from experimental evidence.¹² Chemical processes which occurred during melting affected the ratio of soda to potash, but the total molar content of these alkalis in the glass remained similar to their content as carbonates in the batch. The final concentrations of magnesia and lime were unchanged (Tanimoto and Rehren 2008: 2571).

Another possible variable in the nature of plant ashes was demonstrated by Smedley and Jackson (2006; Jackson and Smedley 2008) when they measured the changes in yield weight and in the composition of bracken during its growth cycle. The compositional differences in glasses made with ashes from plants harvested at different times during the growth cycle has implications for the interpretation of archaeological glass compositions, and although bracken was not used to make Near Eastern glasses, the principle of these findings should be considered in the study of Near Eastern plant ashes.

Further work on plant ash compositions was published by Tite *et al.* (2006) in which they analysed plant ashes, mostly from the *Salsola kali* plant, from different locations in the Middle East and beyond, but the ash compositions did not match the composition of Egyptian glasses. The suitability of ashes for the production of ancient glass was assessed by calculating and comparing soda to potash ratios (see also Brill 1970a: 110), lime and magnesia contents against total alkali ($\text{CaO} + \text{MgO}/(\text{Na}_2\text{O} + \text{K}_2\text{O})$), and the percentage of alkali present as carbonates (Tite *et al.* 2006: 1286) for both ashes and selected ancient glasses. Similarly,

(1997).

¹² For recent experimental work on the melting characteristics of glasses made from vegetable ash and sand mixtures see Jackson and Smedley (2004). Although these were potash rich ashes, the study is interesting because it showed how the choice of alkali could affect the melting temperature of the batch.

Rehren (2008: 1345) advocated the characterisation of the plant ash component of glasses by using the ratios of soda to potash, lime to magnesia, and total alkali oxides to total alkali earth oxides.

A variety of plant ashes specifically from Syria was studied by Barkoudah and Henderson (2006) who provided new chemical data for ash compositions, and canvassed the issues of variability of composition and of relating ash composition to final glass compositions. They found a number of sodium-rich plant ashes, and claimed that the positive correlation between magnesium, potassium and calcium in plants of the *Salsola* genus helped to confirm its use in ancient glass production on the grounds that such correlations are found in some ancient plant-ash glasses, although the absolute concentrations of alkali in the ashes of these plants could be argued to be insufficient to have been used to make LBA glass. The results of Barkoudah and Henderson's study indicate that the same plants grown in different locations have different compositions (2006: 306-310), supporting Brill's earlier finding (1970a: 110).

Despite the variability of plant ash composition, the ancient glass produced from it was of a relatively consistent composition, within geographical and chronological limits (Rehren 2000a), although how this was achieved remains unclear, as do the relationships between the compositions of plants, their ashes and the glasses produced from them (Freestone 2006: 205; see also Shugar and Rehren 2002; Jackson *et al.* 2005; Tite *et al.* 2006). Nicholson and Henderson (2000: 197) argued that if the first glass-makers were brought to Egypt from Mitanni, they might have used plants for ashing that were similar to those in their native land, presumably ensuring a certain similarity of composition to those glasses made in the Near East.

The issues of compositional variability of plants and their ashes, which occur for a number of reasons, and the translation of elemental concentrations from ashes to final glass, continue to occupy researchers and to inform our understanding of the complexities of raw material selection and the sophistication of the art of ancient glass-making.

1.9 Mineral Soda

Mineral soda was used as an alternative to a plant ash source of soda flux to make ancient glasses in the IA. Glasses of the LMLK type are considered to have been made using a mineral soda source, most widely believed to be natron,¹³ or trona, the naturally occurring sodium

¹³ The term 'natron' refers to a particular mineral, and so the non-specific terms 'mineral soda' or 'natron-type' are often used in preference (see Freestone 2006: 204) and are interchangeable with it in the present study.

carbonate/ sodium bicarbonate (Na_2CO_3 , NaHCO_3) found in the Western Desert oases of Egypt, such as the Wadi Natrun (Shortland 2004).¹⁴ Natron was used also in making soap and in embalming (Nicholson and Henderson 2000: 216). Turner (1956c: 282T-291T) investigated the sources of alkali salts, and natron in particular, as the most likely mineral soda source used in ancient glasses of low alkali content, noting its complex and variable composition.

Sayre and Smith (1967: 290) analysed the composition of natron salts from 11th and 18th Dynasty tombs to show that it had a low concentration of both potash and magnesia (in the order of 0.1%) and hence would not have contributed these oxides to the glasses. They concluded that HMK glasses could not have been made with natron, but rather with plant ashes or, less likely, evaporated river water (Sayre and Smith 1967: 289-291), as suggested by Turner who returned similar findings from his analyses of natron from 18th Dynasty tombs and from the Wadi Natrun (1956c: 283T-284T). The analyses of natron by Bezborodov (1975: 56), Brill (1999b: 480), Shortland (2004) and Shortland *et al.* (2006: 525) have confirmed the composition and relatively uncontaminated nature of natron as characterised in the previous studies.¹⁵

Until recently, it has been thought that glass of the natron-type was dominant in the Mediterranean and surrounding regions from the mid-1st millennium BC through to the late 1st millennium AD (Smith 1963; Sayre and Smith 1974: 58). Shortland *et al.* (2006) traced the history of the use of natron as a flux in ancient vitreous materials noting that there was no conclusive evidence for the use of natron as the main flux in 2nd millennium BC glasses, but it appears to have been introduced as early as the 10th C BC in the glasses from the Egyptian tomb of Nesikhons (Schlick-Nolte and Werthmann 2003; section 1.5).

1.10 Colourants, Opacifiers and Decolourants

Ancient glasses were modified with a wide range of additives which imparted colour, made naturally translucent glass opaque or decoloured naturally tinted glass to achieve a colourless product.

Early studies of ancient Near Eastern and Egyptian glasses recognised copper as a common colouring agent which produced blue, green and opaque red glasses,¹⁶ and cobalt was identified as a dark blue colouring agent in both Egyptian and Babylonian glasses, although it was used less frequently than copper and its source was unknown. Manganese was identified as a purple or black colouring agent,¹⁷ and antimony as a refining agent in glasses (Farnsworth and Ritchie 1938: 159-164; Turner 1956a; 1956b: 179T).

Studies since then have focussed on the chemistry of colourants, decolourants and opacifiers, which because of the availability of more sensitive analytical techniques, are able to be measured in increasingly small quantities, thereby allowing detailed characterisation of the colourant components of ancient glasses. This in turn helps to relate the analysed glass compositions to possible raw materials. Recently, the nature and uses of individual colourants and opacifiers have been conveniently summarised by Nicholson and Henderson (2000: 217-218) and Shortland (2002: 517-519), amongst others. Although these summaries were based on Egyptian LBA glasses, they are equally applicable to LBA Near Eastern glasses. In addition to those colours mentioned above, glass was made in the following colours; calcium antimonate which produced white, lead antimonate which produced yellow, and a mixture of copper blue and calcium antimonate which produced a turquoise opaque colour, cobalt blue and calcium antimonate made a dark opaque blue and lead antimonate yellow and copper together created an opaque green, and iron oxide present from 0.3% to 1.5% would have imparted a greenish hue to glass (Schreurs and Brill 1984: 199). Dark brown or amber could also be produced by the presence of iron oxide in combination with sulphur (Schreurs and Brill 1984: 199, 206-207; Nicholson and Henderson 2000: 217).¹⁸ In the IA, antimony was used for both decolouring and opacifying glass (Brill 1999b: 47), while iron in sufficient quantity (usually in excess of 5% iron oxide) produced a dark green to black coloured glass (Stapleton and Swanson 2002b: Table 1).

The presence of tin in some blue glasses from Malkata and Lisht suggested the use of the by-products of bronze-making and working to Mass *et al.* (2002: 67, 69). Shortland (2005: 2) commented that the ratio of tin to copper, in the order of 1:10, indicated the derivation of these elements from bronze. Egyptian copper blue

¹⁴ The locations of possible natron sources around the Dakhla and Kharga oases were considered by Shortland (2004) and Shortland *et al.* (2006), who analysed specimens for composition. Trona was also sourced in antiquity from the Beheira province in Lower Egypt (Nicholson and Henderson 2000: 216).

¹⁵ Degryse *et al.* (2005: Table 6) analysed lacustrine salt patches near Sagalassos in southern Turkey as possible sources of mineral soda for the Roman and Byzantine glasses they were studying, and found them to be highly variable in their contents of soda, magnesia, potash and lime.

¹⁶ Red glasses are not analysed in the present study and will not be discussed here.

¹⁷ The use of manganese as a decolourant in glasses occurred from a later period and thus is beyond the scope of this study, but information on the chemistry of decolouring with manganese can be found in the publications by Weyl (1953: 164-165) and Henderson (1985a: 284).

¹⁸ For further information see Weyl (1953: 91) and Bamford (1982: 6) who explain the chemistry of iron as a colourant.

glasses may contain copper derived from bronze, but this is not the case in copper blue glasses from the Near East, such as in those from Nuzi. This suggests that copper sources were different in the two regions.

1.10.1 Cobalt

Early investigations into the nature of cobalt as a colourant began to recognise elemental relationships which led eventually to the identification of two possible sources of this colourant in the Near East and Egypt. Early work by Farnsworth and Ritchie (1938: 159-164) attributed the dark blue colour of Egyptian 18th Dynasty glasses to the presence of cobalt with associated manganese and copper. They summarised previously published results which reported cobalt to be present in ancient Egyptian glass and glaze. At this time, cobalt was considered to have been deliberately added from an unidentifiable source. Garner (1956a; 1956b) proposed that an Iranian arsenical cobalt ore with low manganese content had been used in a very early non-Egyptian glass from Eridu, dated c.2000 BC. Sayre (1963: 267-268) noted that not only manganese, but nickel and zinc concentrations were enhanced in cobalt blue glasses from Egypt and Mycenae, but that the elemental content was different in two Western Asiatic cobalt blue glasses, which Sayre and Smith concluded must have been because a different source of cobalt was used (Sayre and Smith 1974: 51, 54).

Kaczmarczyk and Hedges surveyed the composition of Egyptian faience from Predynastic to Roman times (1983) and established that the cobalt colourant used in ancient Egyptian New Kingdom vitreous materials was probably derived from the alum¹⁹ deposits of the Western Oases of Egypt, especially the Kharga and Dakhla Oases (1983: 41-55). They noted that the 'striking feature of the occurrence of cobalt in New Kingdom faience is its association with manganese, zinc, nickel and aluminium' (Kaczmarczyk and Hedges 1983: 46). These findings were confirmed by Kaczmarczyk (1986), who analysed Egyptian blue pigments from the 2nd millennium BC, establishing that cobalt was invariably associated with elevated concentrations of aluminium, magnesium, manganese, iron, nickel and zinc in cobalt blue Egyptian glasses, and that the raw material was derived from the Great Western Oases in Egypt.

Kaczmarczyk and Hedges (1983: 45-47) noted the virtual disappearance of cobalt from post-New Kingdom vitreous materials, from the 12th to the 7th C BC, concluding that when it reappeared during the 26th Dynasty in the Late Period (7th C BC), it must have originated from a different ore source, because the

concentrations of manganese, nickel and zinc returned to the average level of impurities, no longer being found at the elevated levels associated with cobalt alum, and there were no clear correlations with other elements. Cobalt in vitreous materials from this time resembled cobalt detected in Mesopotamian pigments of all time periods, which Kaczmarczyk and Hedges assumed were from Iran (1983: 53; Kaczmarczyk 1986: 373-374). The distinction between an Egyptian alum source of cobalt and an eastern, possibly Iranian ore source of cobalt which was used in Near Eastern glasses, was clarified. Their results highlighted to Kaczmarczyk and Hedges just 'how fragmentary and inadequate is the present state of knowledge of 1st millennium B.C. Mesopotamian faience and glass' (1983: 294).²⁰

Analyses of alum from the Western Desert Oases in Egypt proved that it contained the same trace elements, in approximately the same relative amounts as those found in cobalt blue glasses, including relatively high levels of alumina (Kaczmarczyk 1986: Table 34.3; Shortland and Tite 2000: 145-146). Further chemical analyses of Egyptian cobalt alums were published by Shortland *et al.* (2006: 157) and Gratuze and Picon (2005: 272-273) confirming the results of earlier compositional studies, and showing that the levels of soda and lime were comparatively low and that compositions of alums from around the Kharga and Dakhla oases were variable. The unpredictable composition of cobalt alum was noted also by Jackson and Nicholson (2007: 104).

The work of Lilyquist *et al.* (1993: 36, 41-43; Lilyquist and Brill 1996) showed that the Egyptian cobalt blue glasses of the 2nd millennium BC, from as early as the reign of Thutmose III, were compositionally distinct from other contemporary glasses, having high alumina and magnesia contents from the addition of the alum colourant, but with low potash levels. This anomalous composition does not fit the accepted models of HMK (plant ash) or LMLK (natron) glass and has provoked discussion about the alkali source for the Egyptian cobalt glasses. Shortland and Tite (2000: 146-147) suggested that they were made with natron, which explained the low potash levels, while the high magnesia content was due to magnesia in the alum.

Rehren (2001) believed that the cobalt blue glasses were made using a low-potash plant ash of a different type to that used in Near Eastern plant ash glasses, questioning why, if it were a natron-based glass, this technology would have been restricted to the one colour. Rehren preferred the view that LBA glass-making on the whole was based on plant ash alkali sources. Jackson and Nicholson (2007: 112-113) similarly concluded that copper and cobalt coloured glasses were made using

¹⁹ 'Alum' is defined by Shortland *et al.* (2006: 153) as the hydrated double sulphate of aluminium with or without an alkali, alkali earth or transition metal.

²⁰ Henderson (1985a: 278-281; 1989c: 33-36; 2000: 30-32) has summarised the early work on cobalt as a colourant.

different types of plants, one of which was lower in potash than the other. Alternatively, Tite and Shortland (2003: 302) tentatively proposed that cobalt blue glass was made with a mixture of cobalt coloured frit, plant ash and quartz, which explained the lower potash level of the cobalt glass compared with contemporary copper blue glasses, and repeated Shortland's (2000b) finding that the cobalt contents of New Kingdom glasses correlated with alumina, manganese, nickel and zinc, but not magnesia, because of the addition of plant ash containing magnesia. The experiments of Shortland *et al.* (2006: 164) showed that the magnesia content of the alums could vary widely when cobalt, alumina and magnesia were precipitated from the alum.

The results of analyses of Egyptian cobalt coloured glasses and cobalt alums from the only known source in the oases of the Egyptian western desert, show that the cobalt colourant in these high alumina glasses was derived from the cobalt alums, and that the glasses are of an unusual high-magnesia, low-potash type. Brill's analyses of IA cobalt blue glasses from Nimrud also indicate a cobalt colourant associated with elevated levels of the same trace elements (Brill 1999b: 47-48). Various reasons for this composition have been proposed but not satisfactorily resolved.

1.10.2 Antimony as an Opacifier and a Decolourant

Turner and Rooksby published several studies concerning opalising or opacifying agents used in early glasses, for example from Thebes (c.1450 BC) and Nimrud (8th to 6th C BC) (Turner and Rooksby 1959; 1961; 1963; Rooksby 1959; 1962). In these studies, Turner and Rooksby identified antimony in the form of calcium antimonate ($\text{Ca}_2\text{Sb}_2\text{O}_7$ or CaSb_2O_6) as the opacifier for white opaque glasses, and when mixed with translucent copper blue, produced turquoise opaque glasses.²¹ The intentional inclusion of a material such as stibnite (antimony sulphide, Sb_2S_3) was suggested for this purpose, because there are no known mineral forms of calcium antimonate in Egypt or the Near East (Mass *et al.* 2001: 41; Mass *et al.* 2002: 70, 78).²² Opacity resulted from the presence of antimony pentoxide (Sb_2O_5) in the glass (Sayre and Smith 1974: 59).²³

Sayre (1963; 1965) discussed the presence of antimony and manganese in early glasses and concluded that these components were added deliberately either as

decolourants or as opacifiers, with colourless glass being rare in the 2nd millennium BC. He noted that of five colourless Egyptian specimens and three colourless Mesopotamian specimens from 13th C BC Tchoga Zanbil in Iran, none contained large concentrations of either antimony or manganese, indicating that these elements were not used as decolourants in LBA glasses (Sayre 1963: 269). Colourless glasses of the 2nd millennium BC from Egypt, analysed by Bimson and Freestone (two samples) (1988: 12), Wypyski (one sample) (in Lilyquist *et al.* 1993: 36), Shortland and Eremin (ten samples) (2006: 584) and Jackson and Nicholson (one sample) (2007: 182) appear to contain little or no antimony or manganese, supporting Sayre's finding. Decolouring of the glass might instead have been achieved by careful control of the furnace atmospheres (Jackson and Nicholson 2007: 106), or could have been the result of using pure batch materials (Nicholson 2007: 1).

Fossing (1940: 42) noted the consistent appearance of high concentrations of antimony in colourless glasses from approximately the mid-6th C BC, until antimony as a decolourant was largely replaced by manganese at the end of the 1st millennium BC (see also Biek and Bayley 1979: 6). Sayre (1963: 272) found that all 12 specimens of colourless 7th to 1st C BC glasses he analysed contained elevated levels of antimony similar to the levels found in opaque glasses. He explained that the ability of antimony to both opacify and decolour resulted from its presence in the glasses in different states of chemical valence. The tradition of opacifying with antimony was evident from the earliest glasses and into Roman times (Brill and Moll 1963: 299), and the use of antimony as an opacifying agent appears to have led to the discovery that antimony could, under the appropriate conditions, decolour glass (Sayre 1963: 272). Brill (1970a: 116) summarised the use of antimony in ancient times for three distinctly different purposes as either a decolourant, by oxidising iron to render the glass colourless, as a fining agent to remove small seeds or bubbles from the glass, or as an opacifying agent at the levels of approximately 1% to 2% antimony oxide in the glass.

The property of calcium antimonate to act as an opacifier was discussed by Shortland (2002: 519-523) who suggested that during cooling of the melt, antimony combined with the lime thus drawing it out of the batch to form calcium antimonate. This proposal was based on Shortland's understanding at the time that lime levels were lower in opacified LBA Egyptian glasses than in their translucent counterparts. Shortland considered that if calcium antimonate had been added as a preformed material, the lime content would be expected to have risen in opaque glasses and not be reduced.

²¹ Although no yellow opaque glasses were analysed in the present study, it is noted that lead antimonate ($\text{Pb}_2\text{Sb}_2\text{O}_7$) was used to create opaque yellow, and opaque green (Mass *et al.* 2002: 70-71).

²² Mass *et al.* (2002: 70) suggested stibnite as a lead-free antimony source, found throughout the Mediterranean and the Near East, for Roman glasses (see also Mass *et al.* 1998).

²³ Unintentional opacity could be due also to devitrification, incomplete vitrification, many gas bubbles or impurities in the glass (Henderson 1985a: 286).

Nicholson and Henderson (2000: 208) proposed that antimony was added as an opacifier to translucent blue Egyptian glass to make turquoise opaque glass. Shortland suggested that to make opaque blue glasses, antimony could have been added to a translucent blue glass by mixing translucent blue and opaque white glasses (Shortland 2002: 522) at the same time that Mass *et al.* (2002: 78) suggested the addition of ready-made white glass to achieve opacity in Egyptian glasses. Further research by Shortland and Eremin (2006: 591) found that, apart from the antimony levels, the compositions of white and colourless Egyptian glasses were closely similar, including the average lime concentrations, which suggested to them that antimony alone was added to the colourless glass to create white glass.²⁴ Whether antimony or white glass was added to a translucent blue glass to achieve opacity remains unanswered.

1.11 Trace Element Analyses

After early work on ancient glass had 'systematised' knowledge of basic glass compositions and colourants, Brill (1969: 48) looked forward to the 'long hoped-for useful pattern of trace-element concentrations, for example the rare earths'. He encouraged the analysis of

'large numbers of well authenticated specimens of fragments and vessels encompassing a wide range of places and periods. The analyses must be accurate where necessary and comprehensive in terms of elements determined. They must include a large number of specimens to allow statistically significant inferences to be drawn. It is only in this way that a useful catalogue of ancient compositions can be compiled. ... The meaningful variability appears only to be in minor, or trace, or 'trace-trace' elements.'

The difficulty of establishing the origin of ancient glass was noted by Velde and Gendron (1980: 183) who, when referring to previous compositional analyses of glass, commented that 'Chemical analyses of major elements composing the glass itself has not given any great hope of distinguishing one area of production from another', although general compositional groups could be distinguished by a broad chronological period or geographical region, but composition and stylistic criteria were not sufficiently detailed to provide more refined classifications.

²⁴ Recent studies of colourless glasses have involved those predominantly from the Roman period when colourless glass was common (Jackson *et al.* 2003; Jackson 2005b). In some Roman glasses from Britain, Jackson (2005b: 771) has found that both antimony and manganese were present, but that antimony was probably the intended decolourant for the majority of glasses analysed. See also Sayre (1963: 279-280) for the mixed use of manganese and antimony in Rhenish glasses of the 1st millennium AD.

Compositional studies which include trace element analyses have become more frequent with the availability of, and improvement in analytical instrumentation, and have allowed more detailed characterisation and comparison of groups of glasses.²⁵ Freestone *et al.* (2000: 65-82), in their study of glasses of Byzantine and Early Islamic date from Israel, employed ICP-MS to analyse a selection of glasses from Apollonia and Bet Eli'ezer, confirming the grouping of glass based on major element composition, and allowing further discrimination between the glass groups.

Freestone *et al.* (2002) applied ICP-MS and ICP-AES trace element analyses to AD 6th to 7th C glasses from Maroni Petrera in Cyprus, and normalised the data for a selection of elements to the mean composition of the continental crust. This showed which elements were enriched or depleted relative to the crustal values, and indicated the use of a mineralogically pure sand to make the glass. Normalisation of glass data to mean crustal values allowed compositional anomalies to be recognised.

Shortland *et al.* (2007) analysed LBA glasses from Nuzi, Tell Brak and Egypt for 32 trace elements by laser ablation ICP-MS. They advocated the potential of trace element compositional fingerprinting to resolve difficult debates about provenance and details of manufacturing technology. The calculation of the ratios of zirconium to titanium, and of chromium to lanthanum, enabled the authors to discriminate between Egyptian and Near Eastern glass production in the 2nd millennium BC. They showed that elevated chromium contents and high chromium to lanthanum ratios are characteristic of Near Eastern glasses, while Egyptian glasses contain elevated levels of zirconium (Shortland *et al.* 2007: 781, 787-789). This important development has advanced our ability to distinguish the consistent differences between the two regional groups of glass. These differences indicate the use of different raw materials and/or manufacturing processes, because these trace elements provide distinctive geological signatures that vary between regions.

Solution ICP-MS was used by Mirti *et al.* (2008) to analyse 40 major, minor and trace elements, including the REE, of Parthian and Sasanian glasses from Iraq, but their discussion was concerned principally with the base glass and colourant composition with limited reference to the REE and associated elements, the levels of which indicated the use of an impure sand silica source (Mirti *et al.* 2008: 441, 443). Similarly, Santagostino Barbone *et al.* (2008) have studied late 1st millennium BC to

²⁵ Much has been written about the scientific fingerprinting of materials and of artefacts to trace the source of raw materials or places of manufacture, for example, Pollard and Heron (1996), Pollard *et al.* (2007), Brothwell and Pollard (2001: Section 6, 441-518).

AD 1st millennium glasses from southern Italy using ICP-MS, amongst other techniques, to produce a suite of 54 oxides and elements, including the REE. Their discussion centred on the main colourants with only brief reference to their trace element data (Santagostino Barbone *et al.* 2008: Table 2, 460).

The collection of detailed compositional data to answer archaeological questions about the technology, organisation and recipes for glass production, including the nature, sources and craftsmen's choices of raw materials, and the geographical and chronological distribution of raw materials, raw glass and finished glass objects, is being made possible by the development of sensitive analytical techniques such as ICP-MS, with 'interpretation...becoming the central challenge' (Lilyquist and Brill 1996: 8).

The published chemical analyses (as at 2009) of selections of glasses from the LBA and IA Near East and LBA Egypt are compiled in the following sections. These studies form part of the growing data-base of compositional information that scientists, technologists and archaeologists alike use to try to unravel the details of ancient glass production.

1.12 Analyses of LBA Near Eastern Glasses

The early chemical investigations of glass composition should be viewed with caution because these analyses, assembled by Turner (1956b), involved small numbers of samples, often of uncertain context and date, and were performed using techniques that were subject to error and were inadequate by comparison with current analytical instrumental methods (Bimson 1987: 165-166). Smith (1963: 286) made the significant observation that well-dated samples are of 'extreme importance to a research program', but acknowledged that for various reasons this was not always possible. Archaeological contexts have not always been well recorded and relatively few Near Eastern glasses have been chemically analysed. Moreover, the data from the published studies have not been brought together and examined as a whole and consequently our understanding of the LBA glass industry remains fragmentary. Investigating the technological history of glass is, as Moorey (1985: ix) put it, 'not so much a matter of absent evidence, a problem not to be underestimated, as of scattered and incoherent source material which has never been examined'. Moorey compiled available information from early Near Eastern glass studies in an historical survey of early glass-making which did much to clarify the context and chronology of excavated glasses (Moorey 1985; 1999).

Recent analyses of LBA Near Eastern glass compositions have been made by several researchers in an attempt to learn more of the nature of these early glasses and

the raw materials used in their manufacture. Unusually early glasses from Dinkha Tepe in Iran, c.1800 to 1600 BC, were analysed by McGovern *et al.* (1991) and found to be coloured blue with copper. Glasses from 14th C BC Tell Brak in northern Syria have been analysed for composition by Brill and Shirohata, by Velde and by Henderson (in Oates *et al.* 1997: 89-94, 94-100; Brill 1999b: 39), by Shortland and Eremin (2006: 595) and by Shortland *et al.* (2007: 784). Brill (1999b: 40-41) and Vandiver (1982: 84; 1983: 239-247) have analysed glasses from 15th to 14th C BC Nuzi, as have Shortland and Eremin (2006: 595) and Shortland *et al.* (2007: 784) since the present study of glasses from Nuzi was begun. The chief purposes of the latter two studies were, first, to provide a comparison for Egyptian glass compositions rather than to investigate in any detail the compositions of the Mesopotamian glasses themselves and, second, to answer questions about where and how widespread glass-making was in the 2nd millennium BC, whether workshops were specialising in particular colours and whether local or imported raw materials were being used. Brill has analysed a selection of glasses from Mesopotamian Tell al-Rimah of the 15th to 13th C BC (1999b: 42-43), and 13th C BC Tchoga Zanbil in Iran (1999b: 45). Brill's (1999a; 1999b) collected data from the analyses of a variety of glasses were published, but without interpretation, nevertheless providing an invaluable tool for future compositional work.

McGovern and co-workers examined silicate industry development, the origins of the glass industry in the region of Syria-Palestine in c.1600 BC, and craft interaction between Egypt and the Levant, especially with reference to the vitreous materials found at the site of Beth Shan in Israel, and in the Baq'ah Valley in Jordan (McGovern 1980; 1985; 1986; 1987b; 1995; Swann *et al.* 1989; McGovern *et al.* 1993; James and McGovern 1993; 157). They used the PIXE-PIGME technique to analyse the compositions of the 13th C BC vitreous materials from Beth Shan, but an inter-laboratory comparison of the results for the PIXE-PIGME they used with results from the SEM-EDS system at the British Museum suggested that serious errors occurred in the PIXE-PIGME analysis (Freestone, personal communication).

In general, LBA Near Eastern glasses are remarkably homogeneous in base glass composition being HMHK glasses, many of which are coloured copper blue. The location and number of production centres is unknown, but the industry appears to have used well-controlled raw materials of similar composition.

1.13 Analyses of LBA Egyptian Glasses

Much research has been undertaken on Egyptian glasses, which provides comparative material for the present study and will be reviewed briefly in this section. Studies of Egyptian glasses by many of the

early researchers have been referred to in previous sections of this chapter. These studies provided general information on the composition of 2nd millennium BC Egyptian glasses and contributed to the current understanding of their chemistry. An archaeological overview of Egyptian glass from the earliest occurrences to the Graeco-Roman period has been published by Nicholson (1993).

Bimson and Freestone (1988: 11-15) analysed the base glass and colourant components of several early glasses from the reign of Queen Hatshepsut (1473-1458 BC) and the Amarna period (1353-1333 BC). The use of cobalt as a colourant was discussed, and the colourless glasses were found to contain no manganese or antimony, indicating that these elements had not been used for decolouring ancient glasses (section 1.10.2). Analyses of glasses from Amarna, Malkata, Lisht, Timna and Wadi Qirud have been analysed and collectively published by Brill (1999b: 27-37; see also Brill and Barnes 1988). The chemical analyses of 2nd millennium BC glasses performed by Wypyski (Lilyquist *et al.* 1993: 36-39) categorised early Egyptian glasses from the reigns of Hatshepsut to Thutmose IV, and were grouped as 'pre-Malkata' glasses. This chemical archaeological study was prompted by the authors' observation that previous compositional analyses of Egyptian glasses had been concerned with raw materials, opacifiers and colourants and were based on few samples broadly dated to the Malkata and Amarna periods of the late 18th Dynasty. Wypyski and Brill (Lilyquist *et al.* 1993: 36-39) filled in the 150-year gap prior to this time and included Brill's, at that time, unpublished analyses of Amarna, Malkata and Nuzi glasses. Both Brill's and Wypyski's analyses, and their regional comparative approach to the study of early glasses have remained as a standard for compositional comparisons with other glasses from Egypt and the Near East. Much of the glass that they analysed was of the HMK type and provides interesting comparative material for contemporary Near Eastern glasses.

Egyptian LBA glasses were analysed by Shortland and Tite (2000) who determined that there were both copper blue plant ash glasses and cobalt coloured 'natron' glasses used in Egypt at this time. The focus of the work by Mass *et al.* (2002) was on the colourant elements and opacifying agents of the Malkata and Lisht glasses, which included copper blue glasses, and were of a soda-lime-silica type made with plant ash.

Analysis of 226 LBA glasses from Egypt and Mesopotamia was carried out by Shortland and co-workers (Shortland and Eremin 2006: 581-603; Shortland *et al.* 2007: 781-789) in a two-part study which focussed primarily on the identification of elements brought in with each of the raw materials, and the characterisation of those raw materials. They followed the proposition that

different glass-making sites in Egypt and the Near East would have used local raw materials with identifiable chemical variations that provided the opportunity for provenancing the glass.

Shortland and Eremin (2006: 591-593) summarised the nature of the colourants used in the glasses they analysed, and for opacified glasses concluded that antimony must have been added as an individual ingredient because the base glass compositions of white and colourless glasses were otherwise closely similar. Manganese was added as a relatively pure ingredient to colourless glass to create purple (section 1.10). They observed that none of the early copper blue glasses from the reigns of Thutmose III to Amenophis II contained a significant level of tin, whereas tin in the copper blue glasses from Amarna was usual at levels that indicated the use of bronze scrap as the colourant source. Based on this finding, they have suggested that the early low-tin, copper blue glasses originated in Mesopotamia, a region from which glasses were revealed by chemical analysis to contain insignificant levels of tin (Shortland 2005: 1-5). Mass *et al.* (2002: 67, 69, 75) found the presence of tin in some blue glasses from Malkata and Lisht which suggested the use of a bronze by-product.

Shortland and Eremin (2006: 596-598) observed inconsistency in the concentrations of lime between the glasses they analysed from the early or 'pre-Malkata' and the Malkata/Amarna periods, by comparison with those from mid-13th C BC Lisht. The similarity of magnesia and potash content in all glasses, combined with the variation in lime levels, led the authors to propose that the same source of plant ash was used for all three groups of glass and that the lime levels were adjusted by the deliberate addition of lime (section 1.7).

The general similarity of Mesopotamian glasses from Nuzi and Tell Brak to those from Egypt were noted, although ICP-MS analyses showed that they were probably of distinct compositions. The value of the low detection limits of ICP-MS were acknowledged as the most sensitive method for provenancing glass by examining the transition and trace elements (Shortland *et al.* 2007). Shortland *et al.* (2007) recognised that trace elements and their ratios could be used to discriminate between Egyptian and Near Eastern glasses of the LBA (see also Shortland and Eremin 2006: 596-598).

The publication by Nicholson (2007) of comprehensive investigations at the 14th C BC site of Amarna provided new compositional analyses of glasses (Jackson and Nicholson 2007: 100-116; Appendix 5) and a detailed and informative discussion of Amarna's important role in early Egyptian glass production, drawing together the results of excavation, experiment, previous research and materials analysis in the wider context of the New

Kingdom vitreous materials production to provide convincing evidence that Amarna was indeed a glass-making site.

The 2nd millennium BC glass production site of Qantir-Piramesses in the Egyptian delta has been investigated by Rehren and Pusch (1997; 1999; 2005; Rehren *et al.* 1998; 2001; Pusch and Rehren 2007) and, most recently, a discussion of the glasses from the LBA site of Qantir-Piramesses, including a small selection of compositional analyses of glasses associated with glass production materials, have been published by Schoer and Rehren (2007). Rehren and Pusch (2007) experimented with the pounding and grinding of quartz stones to determine the extent to which the grinding tools contaminated the silica by leaving a trace element signature in experimental glasses. They found that the pattern of contamination in the ground material was the same as in the grinding tools, a consideration when interpreting the trace element data from analyses of ancient glasses. The factors that affected the final glass composition, including raw material types and sources, contamination of the batch throughout the glass production process, the choice of batch recipe and firing regime and chemical reactions which occurred during firing, have been summarised by Rehren (2008: 1350).

From their work on the ancient Egyptian glass industry at Qantir, Rehren *et al.* (2001) proposed a model for LBA glass production and working which stated that while common colours, such as copper blue, were produced at a number of sites in the Near East and Egypt, specific colours were produced only at specialised sites which were dependent on particular raw materials. Long distance trade allowed these colours to be used in many different centres, along with the commonly produced glass colours.

1.14 Analyses of IA Glasses

Few IA glasses have been analysed and no work has been done to compile and interpret the Near Eastern IA assemblage as a whole in its chemical, geographical and chronological contexts. Previous chemical analyses of IA glasses include those of glasses from Hasanlu by Stapleton and Swanson (2002a; 2002b), Stapleton (2003) and Brill (1999b: 43-44), 12th to 11th C BC glasses from Marlik Tepe in Iran,²⁶ one 8th C BC sample from Altin Tepe in Iran, and 9th to 8th C BC glasses from Nimrud by Brill (1978; 1999b: 45, 47-49, 52) and two by Turner and Plenderlieth (Turner 1954: 449T, 455T; 1955: 61, 67).

A brief examination of the limited published data reveals that IA object forms and colours exhibit some

differences to those of LBA glasses, and although more widespread were still limited. There was an increase in the use of strong dark colours, which could appear black, and in the number of colourless and transparent glasses, indicative of the significant variations in chemical composition that were beginning to occur (section 1.2).

1.15 Glass Raw Materials in Brief

Ancient Near Eastern glasses were typically of a soda-lime-silica or high alkali base composition. Soda was the chief alkali flux for the silica, being derived from either plant ashes, which brought with them magnesia, potash and lime, or mineral soda such as natron, which was of relatively pure composition. It is generally believed that pure sand or quartz would have been combined with plant ash, or mineral soda with a lime-rich sand, in the widely accepted two-component model of ancient glass-making. It has long been argued whether the addition of lime, a key constituent which stabilised glasses to prevent dissolution, was intentional or accidental.

Colours were produced by the addition of metal minerals such as cobalt, copper, manganese and iron, and the transparency of the glass was reduced by adding antimony as an opacifying agent, which combined with lead or calcium in the glasses to form opaque yellow or opaque white glasses respectively. Opaque turquoise glass was probably made by adding antimony to translucent blue glass. Copper blue glasses were ubiquitous, having been excavated throughout the Near East and Egypt, while colours such as cobalt blue, black, red, yellow, purple, brown and white are much rarer, perhaps having been produced at specialist workshops.

Current knowledge suggests that antimony was used to decolour glasses from the mid-1st millennium BC, whereas analyses of the limited number of colourless glasses made before this time show that decolouring was achieved without the addition of a decolourant.

HMHK glasses were prevalent in the LBA in Egypt and the Near East, and LMLK glasses have their earliest known occurrence in Egypt in the 10th C BC. The Egyptian cobalt blue glasses have an anomalous composition of high magnesia and low potash but whether this can be attributed to an alum plus plant ash mix, or an alum plus natron mix, remains unclear.

1.16 Aims

While considerable advances had been made in the knowledge of ancient glass-making at the beginning of this project, information on the nature and extent of LBA and IA Near Eastern glass production was still

²⁶ While this is strictly a 2nd millennium date, it falls into the Near Eastern IA.

disjointed and limited, and the distinctions between LBA Egyptian and Near Eastern glass production were rudimentary and not well defined. There had been considerably more work done on Egyptian glasses than on their LBA Near Eastern counterparts, and little work had been done on Near Eastern glass from the IA. This study was designed to address questions regarding the nature of glass from the Near Eastern region from the mid-2nd to mid-1st millennia BC through the acquisition and interpretation of a substantial and unprecedented collection of chemical compositional data. This data can be used to make detailed, systematic comparisons of glasses from the LBA and from the IA, and between the LBA and IA glasses. Comparisons between the data from the present study and from published data can be made to improve our understanding of early glass-making.

The following questions have been considered. What is the chemical nature of LBA and IA glass from the Near East? How do LBA and IA Near Eastern glasses compare chemically with New Kingdom Egyptian glasses? How does IA glass production compare with that of the preceding LBA? Did LBA glass-making practices continue into the IA, or were there innovations in glass production which might be reflected in glass compositions and the choice of raw materials? How did the use of plant ash and mineral soda for fluxing the glass batch develop at this time? How were additives such as colourants and opacifiers used in the IA compared with the LBA? Can long distance trade or the movement of raw materials and/ or finished glasses be identified by the characterisation and comparison of the compositions of glasses from different regions, and by the identification of glass raw ingredients?

LBA glasses from Pella and Nuzi, analysed in this study, typify the earlier glass compositions from the 2nd millennium BC, and early 1st millennium BC glass beads from Pella provide information on glass-making during a time when the decline in glass production has been noted (section 1.2). The 9th to 8th C BC glasses from Nimrud provide information on the later, more wide-ranging IA glass compositions available in the Near Eastern region. In this way, a continuum of production can be traced from the earliest glasses of the mid-2nd millennium BC through to the fall of Nimrud in the late 7th C BC.

The present study aimed to draw together the threads of LBA and IA glass production through examination and interpretation of the compositions of the glasses with regard to the possible raw materials used in their manufacture. In this way, the analyses undertaken in the current study complement and build upon those already published, and provide new insights into LBA to IA glass manufacture in the Near East. It is intended by this process of synthesis of new and existing

information to define the differences and similarities between identifiable glass chemical types from both periods, and between the two periods, in an attempt to provide a better understanding of the development of the earliest glass production in this region and to identify, where possible, trade in raw materials and glass objects.

This study was designed to provide detailed information from the compositional analyses of LBA and IA glasses of the Near East to allow for comparison with other studies, to add to our understanding of the development of the technology of glass-making, and to identify continuity and change in this key period of the history of glass production leading up to the established traditions of the later and far-reaching Hellenistic and Roman glass-making industries. This study represents the first attempt to provide detailed compositional data for a large number of IA Near Eastern glasses, and to compare these data with those from the analyses of other IA and LBA glasses of the Near East.

To answer the questions posed about the development of glass-making during these times, chemical characterisation of the compositions of selected Near Eastern glasses was undertaken using a combination of techniques which provide the most reliable, precise and accurate analyses of the widest range of elements possible at the time. Scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDS), electron probe micro-analysis (EPMA) and solution inductively coupled plasma mass spectrometry (ICP-MS) were selected because of their sensitivity and availability (Chapter 2).

Baxter *et al.* (1995: 140) commented that many glass data-sets that had been studied previously contained small numbers of samples with few measured elements or variables. Instrumental methods such as ICP-MS are capable of producing large data-sets containing a large number of variables for many samples. Baxter *et al.* (1995: 140) suggested that 'the analysis of compositional variation within typological groups is a potentially illuminating way of looking at the data that complements, and may even be more informative than the inspection of mean compositions'. It was anticipated that, in the present study, the recording and handling of the chemical data of a large number of oxides and elements analysed from 132 glass samples would require the development of an innovative system for organising this data in a comprehensive, systematic way which facilitated its study and interpretation. Such a large collection of data from the analyses of eight oxides and 44 elements, including the rare earth elements, from different glass types over a broad chronological period has not been presented in one study previously.

It is anticipated that this compilation of data will enhance and facilitate comparisons with glass compositions from Egypt and from other historical periods to refine and deepen our knowledge of the growth, development and spread of glass-making, the raw materials of glass production and the implications of this information for the appreciation of the sophistication and organisation of the craftsmen who produced a technologically complex, valuable material.

The specific aims of the present study were:

1. to develop a method for reporting and manipulating the compositional data of in excess of 50 elements and oxides analysed from ancient glasses that should facilitate the meaningful grouping and interpretation of the data;
2. to obtain detailed and sensitive characterisation of the chemical composition of a range of LBA and IA glasses from the Near East using SEM-EDS, EPMA and solution ICP-MS as a means to define the glass compositions of each period;
3. to compare the compositions of LBA and IA glasses analysed in the present study to describe the nature and development of glass production and the use of raw materials from the earliest recorded industry, through change and innovation into the mid-1st millennium BC;
4. to assess the LBA and IA glass compositions in the context of recent research into raw materials with particular reference to the nature of the fluxes, colourants and decolourants and, where possible, to further current understanding of the types of raw materials chosen by the early glass manufacturers;
5. to examine and interpret the chemical data obtained from the present study together with comparable data from published studies of glasses of the 2nd and 1st millennia BC, to gain an improved understanding of the regional and chronological characteristics of the earliest glass production, and
6. to identify the possible distribution of glass-making ingredients and/ or finished glass objects.

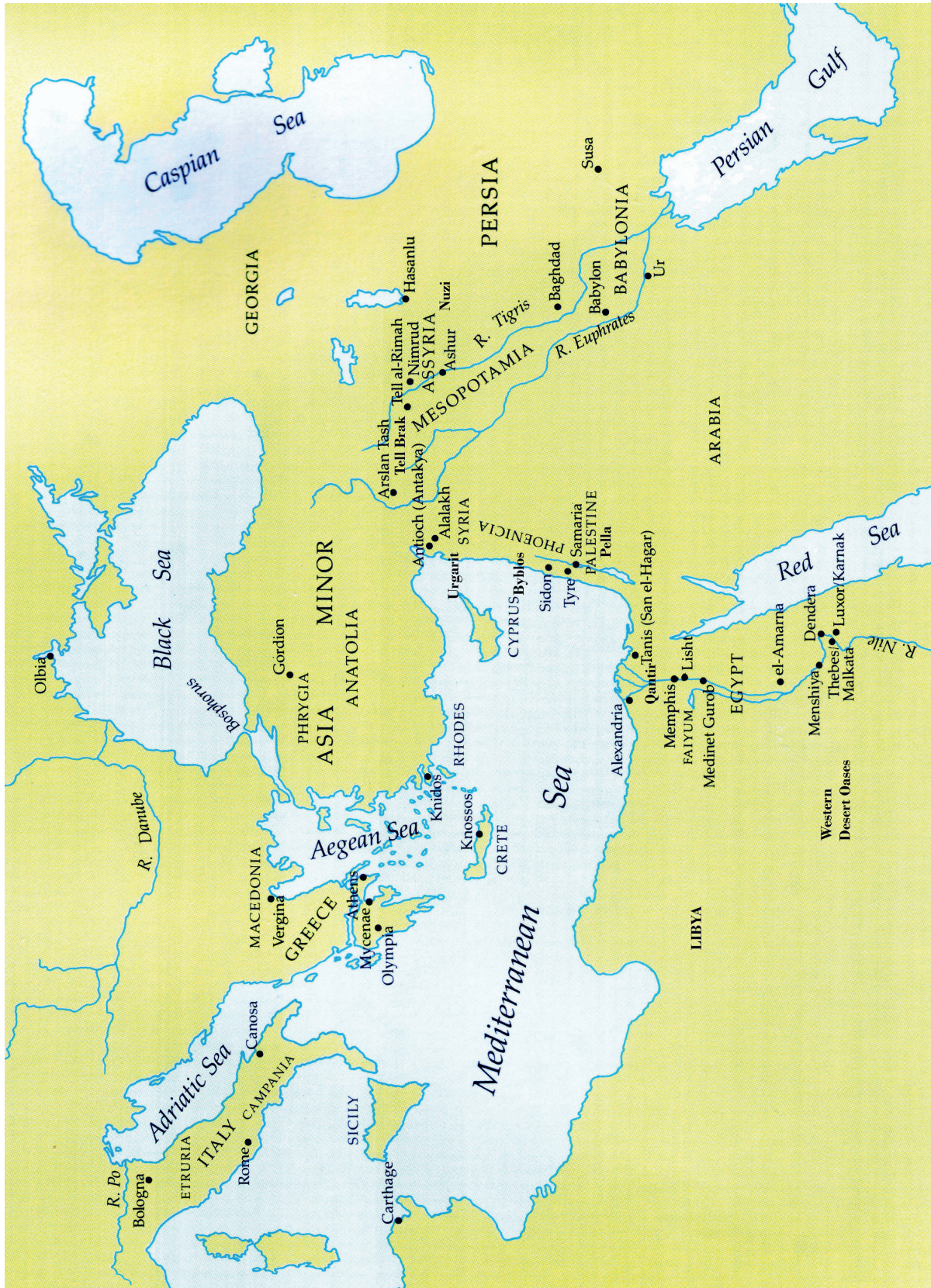


Figure 1-1 Map of the eastern Mediterranean region. Adapted from Tatton-Brown and Andrews 1991: 2