

Contents

List of Contributors	xix
Preface	xxiii
1.1 What is Glass?	1
1.1.1 Introduction	1
1.1.2 Fundamentals of the Glassy State	2
1.1.2.1 Transition Temperature	2
1.1.2.2 General Characteristics of Glasses	3
1.1.2.3 Definition of Glass	3
1.1.2.4 Criteria on the Formation of Glasses	3
1.1.3 Chemical Classification of Glasses	7
1.1.3.1 Silicate Glasses	7
1.1.4 Properties of Glasses	9
1.1.4.1 Glass Behaviour during Heating	9
1.1.4.2 Mechanical Behaviour	13
1.1.4.3 Optical Behaviour	16
1.1.4.4 Chemical Behaviour	18
References	21
1.2 Raw Materials, Recipes and Procedures Used for Glass Making	23
1.2.1 Introduction	23
1.2.1.1 Sources of Information on Ancient Glass Technology	23
1.2.2 Other Sources of Information on Ancient Glass Production Technology	25
1.2.3 Raw Materials of the past	28
1.2.3.1 Vitrifiers	28
1.2.3.2 Fluxes	29
1.2.3.3 Stabilizers	30
1.2.3.4 Fining Agents	31
1.2.3.5 Opacifiers and Colouring Opacifiers	31
1.2.3.6 Colourants	32
1.2.3.7 Reducing Agents	32
1.2.4 Composition Characteristics of Ancient Glass Varieties	32
1.2.5 Present-Day Raw Materials (from the Nineteenth Century Onwards)	34
1.2.5.1 Vitrifiers	34
1.2.5.2 Fluxes	34
1.2.5.3 Stabilizers	34
1.2.5.4 Fining Agents	35
1.2.5.5 Opacifiers	35

1.2.5.6	Colourants	35
1.2.5.7	Approximate Compositions Typical of Some Present-Day Industrial Glass	35
1.2.6	The Melting Process of the past	37
1.2.6.1	The Frit	37
1.2.6.2	The Melting Process	37
1.2.6.3	Primary Glass Production from Raw Materials and Secondary Glass Production by Re-Melting Cullet	37
1.2.6.4	Glass Furnaces of the Past	39
1.2.7	Glass Furnaces of Today	43
	References	45
1.3	Colouring, Decolouring and Opacifying of Glass	49
1.3.1	Introduction	49
1.3.1.1	Physical Principles of Colour and Examples in Ancient Glass	50
1.3.1.2	Physical Principles of Decolouring and Examples in Ancient Translucent Glass	57
1.3.1.3	Physical Principles of Opacifying and Examples in Ancient Opaque Glass	59
1.3.2	Conclusion	63
	References	64
1.4	Glass Compositions over Several Millennia in the Western World	67
1.4.1	Making Silica-Based Glass: Physico-Chemical Constraints	67
1.4.1.1	Melting Minima	67
1.4.1.2	Melting Agent Sources	67
1.4.1.3	Silica Sources	68
1.4.2	Evolution of Glass Compositions	69
1.4.2.1	Initial Stages: Near East (Egypt and Mesopotamia) and Elsewhere 1700 B.C.–300 A.D.: Sodic Plant Ash	69
1.4.2.2	Clear Glass and Blown Glass: the Hellenistic–Roman Period	70
1.4.2.3	Soda from Plant Ash in the Mediterranean Area: ‘Islamic’ Compositions	71
1.4.2.4	Transition to Potassio-Calcic Glass	71
1.4.2.5	Wood Ash Compositions	73
1.4.2.6	Lead Glass	75
1.4.2.7	Back to Sodic Plant Ash	75
1.4.2.8	The Modern Era	75
1.4.3	Summary	75
	References	76
2.1	X-Ray Based Methods of Analysis	79
2.1.1	Introduction	79
2.1.2	X-Ray Analysis Employing Table-Top Instrumentation	80
2.1.2.1	Basic Principles	80
2.1.2.2	X-Ray Fluorescence Analysis	88
2.1.2.3	XRF Instrumentation: EDXRF and WDXRF	92
2.1.2.4	X-Ray Diffraction	107
2.1.2.5	Tomographic X-Ray Imaging	112

2.1.3	X-Ray Methods of Investigation Available at Synchrotron Facilities	113
2.1.3.1	Synchrotron Radiation	114
2.1.3.2	Local and Imaging Analyses Based in X-Rays	115
2.1.3.3	X-Ray Microfocusing Optics	115
2.1.3.4	X-Ray Fluorescence Microprobe Stations	117
2.1.3.5	X-Ray Absorption Spectroscopy	118
2.1.3.6	X-Ray Diffraction	121
2.1.3.7	SR-Based X-Ray Tomography	123
	References	126
2.2	Electron Microscopy	129
2.2.1	Introduction	129
2.2.1.1	Electron-Based versus Photon-Based Imaging	129
2.2.2	Electron–Matter Interactions	133
2.2.2.1	Electron Scattering	133
2.2.3	Analytical Investigations Using Scanning or Transmission Electron Microscopy	134
2.2.3.1	Secondary Electron Imaging	134
2.2.3.2	Backscattered Electron Imaging	135
2.2.3.3	Cathodoluminescence	136
2.2.3.4	X-Ray and Auger Electron Emission	136
2.2.3.5	Interaction Volume and Lateral Resolution	138
2.2.3.6	Quantitative X-Ray Analysis	139
2.2.3.7	Glass Provenance Studies	142
2.2.3.8	Glass Corrosion Studies	148
2.2.3.9	Environmental SEM	148
2.2.4	Additional Analytical Possibilities Using Transmission Electron Microscopy	150
2.2.4.1	Electron Diffraction	150
2.2.4.2	Sample Preparation	153
	References	154
2.3	Ion-Beam Analysis Methods	155
2.3.1	Introduction	155
2.3.2	Principles of the Methods	156
2.3.2.1	PIXE	156
2.3.2.2	PIGE	159
2.3.2.3	Surface-Sensitive Methods: RBS and ERDA	162
2.3.3	Applications: Bulk Analysis	166
2.3.3.1	Bronze Age Glass from the near East and Egypt	166
2.3.3.2	Greek Glass	166
2.3.3.3	Roman Glass	167
2.3.3.4	Chinese Glass	169
2.3.3.5	Medieval Glass from Northern Europe	170
2.3.3.6	Glass à façon de Venise	170
2.3.3.7	Stained Glass Windows	172
2.3.4	Surface Analysis	172
2.3.4.1	Corrosion Studies	172
2.3.4.2	Monitoring of the Corrosion Layer	172

2.3.4.3	Differential Techniques	175
2.3.4.4	Surface-Modified Glass	178
2.3.5	Conclusion	179
	References	180
2.4	Application of Neutron Activation Analysis to Archaeological Studies of Natural and Man-Made Glasses	185
2.4.1	Introduction	185
2.4.2	Theory of Activation Analysis	185
2.4.2.1	Nuclear Reactions	186
2.4.2.2	Reactor Neutron Spectrum and Reaction Cross-Sections	187
2.4.2.3	Radioactive Decay	190
2.4.2.4	Radionuclide Production	191
2.4.2.5	Special Conditions for NAA	191
2.4.2.6	Calculating Concentrations	192
2.4.2.7	Standard Reference Materials and Quality Control Monitors	193
2.4.2.8	Advantages and Disadvantages of NAA	194
2.4.3	Application of NAA to Obsidian	194
2.4.4	Application of NAA to Man-Made Glass	195
2.4.5	Conclusions	197
	Acknowledgements	197
	References	197
3.1	Glass Characterisation Using Laser Ablation Inductively Coupled Plasma Mass Spectrometry Methods	201
3.1.1	Introduction	201
3.1.2	Instrumentation	202
3.1.3	Analytical Procedure and Parameters	204
3.1.4	The Mass Spectrometer	204
3.1.5	The Laser Ablation	205
3.1.5.1	Laser Pulse Repetition Rate	205
3.1.5.2	Ablation Spot or Line	206
3.1.5.3	The Analytical Menus	206
3.1.6	Calculation of Concentrations	209
3.1.7	Interferences, Detection Limits, Reproducibility and Accuracy	209
3.1.8	Examples of Results Obtained by Using Different Analytical Procedures	210
3.1.8.1	Single Spot Analysis	210
3.1.8.2	Line Analysis	218
3.1.8.3	Depth and Surface Profile Analysis	221
3.1.9	Conclusion	232
	Acknowledgements	232
	References	232
3.2	Isotope-Ratio Techniques in Glass Studies	235
3.2.1	Introduction	235
3.2.2	Principles	236
3.2.3	Methodology	236

3.2.4	Isotope Systems in Glass Studies	237
3.2.4.1	Oxygen	237
3.2.4.2	Lead	238
3.2.4.3	Strontium	240
3.2.4.4	Neodymium	242
3.2.5	Perspectives	243
	Acknowledgements	243
	References	243
4.1	Surface Analysis	247
4.1.1	Atomic Force Microscopy (AFM)	248
4.1.1.1	Introduction	248
4.1.1.2	Instrumentation	253
4.1.1.3	Applications	254
4.1.2	Infrared Reflection Absorption Spectroscopy (IRRAS)	258
4.1.2.1	Introduction	258
4.1.2.2	Principles	259
4.1.2.3	Instrumentation	262
4.1.2.4	Applications	263
4.1.3	Secondary Ion Mass Spectrometry (SIMS)	265
4.1.3.1	Introduction	265
4.1.3.2	Principles	265
4.1.3.3	Applications	269
	Acknowledgements	271
	References	271
4.2	Non-Destructive Raman Analysis of Ancient Glasses and Glazes	275
4.2.1	Introduction	275
4.2.2	Fundamentals of Vibrational Spectroscopy	277
4.2.2.1	Vibrations in Crystalline and Amorphous Solids	277
4.2.2.2	The Raman Effect	278
4.2.3	The SiO ₄ Vibrational Unit and an Understanding of its IR and Raman Signatures	280
4.2.4	Polymerisation Degree, Q _n Model and Raman Identification of Glass Types	281
4.2.5	Raman Resonance and Pigment Identification	283
4.2.6	Glass Weathering	285
4.2.6.1	Dating	287
4.2.7	Raman Technique	289
4.2.7.1	On-site Measurements	289
4.2.8	Case Studies	290
4.2.8.1	Trace Phases Probing the Production Process	292
4.2.8.2	Pigments	292
	Acknowledgments	297
	References	297
4.3	The Use of X-Ray Absorption Spectroscopy in Historical Glass Research	301
4.3.1	Introduction	301
4.3.2	Iron and Manganese	302

4.3.3	Copper	305
4.3.3.1	Opaque Glass Slabs and Musive Tesserae	305
4.3.3.2	Red and Blue Glass Beads and Pigments	307
4.3.3.3	Stained Red Glass	307
4.3.4	Calcium, Antimony and Lead	308
	References	308
5.1	Provenance Analysis of Glass Artefacts	311
5.1.1	Introduction	312
5.1.2	Obsidian, a Natural Glass Used since the Paleolithic	312
5.1.3	The First Neolithic Artificial Glassy Materials, and the Discovery of Glass during the Bronze Age	316
5.1.4	When Trade Beads Reached Europe	316
5.1.5	Middle Bronze Age Plant-Ash Soda-Lime Glasses	318
5.1.6	Late Bronze Age Mixed Soda-Potash Glasses	318
5.1.7	Iron Age and Antiquity Natron-Soda-Lime Glasses	321
5.1.8	Protohistoric Glass Trade Routes	321
5.1.9	Glass Chrono-Typo-Chemical Models: a Dating Tool?	321
5.1.10	Glass Trade to and from Central Asia and the Indian World during Antiquity	323
5.1.11	Carolingian Glass Production: Some Unusual Lead Glass Composition Smoothers	328
5.1.12	Late Middle Age Recycled Glass	330
5.1.13	Trade Beads: the Glass Trade Internationalisation, during the Post Medieval Period	336
5.1.14	Conclusion	339
	Acknowledgements	340
	References	340
5.2	Glass at el-Amarna	345
5.2.1	Introduction	345
5.2.2	The Evidence from Amarna	346
5.2.3	Scientific Investigation	346
5.2.3.1	Excavated Evidence from Glass Manufactories	346
5.2.3.2	Finished Glasses	347
5.2.4	Conclusions	350
	References	351
5.3	Evolution of Vitreous Materials in Bronze Age Italy	355
5.3.1	Introduction	355
5.3.2	Materials: Definitions	356
5.3.3	Faiences	356
5.3.4	Glassy Faiences	359
5.3.5	Glass	360
5.3.6	Conclusive Notes and Open Problems	364
	Acknowledgements	366
	References	366
5.4	Black-Appearing Roman Glass	369
5.4.1	Introduction	369

5.4.2	Background	369
5.4.2.1	Roman Glassmaking and Glass Market	369
5.4.2.2	Black-Appearing Glass in Antiquity	370
5.4.3	Origin and Typology of the Analyzed Material	372
5.4.4	Methods of Analysis	373
5.4.5	Results	374
5.4.5.1	Composition of the Glass	374
5.4.5.2	Coloring Agents	376
5.4.5.3	Trace Elements	377
5.4.6	Chronological Evolution of the Recipes Used for Producing Black-Appearing Glass	380
5.4.7	Conclusions and Implications on the General Models for Roman Glassmaking and Distribution	382
	Acknowledgements	384
	References	384
5.5	Glass Compositions of the Merovingian Period in Western Europe	387
5.5.1	Introduction	387
5.5.2	Data Sets Considered	388
5.5.3	Comments	390
5.5.3.1	Fusing Agent	390
5.5.3.2	Silica Source	390
5.5.4	A Special Case	394
5.5.5	Summary	396
	References	396
5.6	Glass in South Asia	399
5.6.1	Introduction	399
5.6.2	The Origin of Glass in South Asia	400
5.6.3	Mineral-Soda-Alumina or m-Na-Al Glass	402
5.6.4	Arikamedu: The Best-Studied Glass-Bead-Making Site in South Asia	406
5.6.5	Discussion	408
5.6.6	Conclusion	410
	Acknowledgements	411
	References	411
5.7	Early Glass in Southeast Asia	415
5.7.1	Introduction	415
5.7.2	Evaluating the Evidence	416
5.7.3	The First Glass Bead in Southeast Asia?	417
5.7.4	Khao Sam Kaeo and Early Southeast Asian Glass	418
5.7.4.1	Archaeological Context and Dating	419
5.7.4.2	Artefact Category	419
5.7.4.3	Assigning Compositional Groups	419
5.7.4.4	Color and the Relationship between Color and Chemical Composition	425
5.7.4.5	Glass Types at Khao Sam Kaeo	425
5.7.4.6	Khao Sam Kaeo: Transferred Technology, Local Adaptation	431
5.7.5	Ban Don Ta Phet	432

5.7.6	The Turn of the New Millennium, Khlong Thom and the Southern Silk Road	433
5.7.6.1	The View from India	433
5.7.6.2	The View from China	433
5.7.6.3	Changes in Southeast Asian Glass Compositions at the Turn of the Millennium	434
5.7.7	Glass Evidence from Khlong Thom	435
5.7.7.1	Primary Glass Production at Khlong Thom	438
5.7.8	Khlong Thom and the Southern Silk Road	439
5.7.9	Conclusion	440
	Acknowledgements	441
	References	441
5.8	Glass Trade between the Middle East and Asia	445
5.8.1	Introduction	445
5.8.2	Portable XRF Suitable for Glass Analysis	446
5.8.3	Asian Glass Beads Excavated from Ancient Tombs in Japan	447
5.8.4	Glass at Shosoin Temple	450
5.8.5	Islamic Glass Excavated from the Raya Site, Egypt	450
5.8.6	The Flow of Islamic Glass to Asia, a Glass Vessel at Toshodaiji Temple	453
5.8.7	The Glass Road to East Asia via the Sea Silk Road	453
5.8.8	Conclusion	456
	References	456
5.9	European Glass Trade Beads in Northeastern North America	459
5.9.1	Blue Beads	461
5.9.2	White Beads	463
5.9.3	Opaque Red Glass	466
5.9.4	Black Beads from Amsterdam	467
5.9.5	Gold-Coloured Beads from Amsterdam	468
5.9.6	Conclusions	469
	Acknowledgements	469
	References	469
6.1	Medieval Glass-Making and -Working in Tuscany and Liguria (Italy). Towards a Standard Methodology for the Classification of Glass-Making and Glass-Working Indicators	473
6.1.1	Introduction	473
6.1.2	Medieval Glass-Making and -Working in Tuscany and Liguria (Italy)	475
6.1.2.1	Archaeological Questions. (S. L. and M. M.)	475
6.1.2.2	Archaeological Evidence of Glass Production Sites in Tuscany: the Elsa Valley (M. M.)	477
6.1.2.3	Archaeological Evidence of Glass Production Sites in Liguria (S. L.)	479
6.1.3	Towards a Standard Methodology for the Classification of Glass Making and Glass Working Indicators	481
6.1.3.1	Methods and Strategies (S. L.)	481

6.1.3.2 The Physical-Chemical Study of Glass-Making and -Working Indicators from the Medieval Glass Factories of Germagnana and S. Cristina (Tuscany) (F. F. and A. P. V.)	486
6.1.3.3 Archaeometric Classification: Results and Discussion	495
6.1.3.4 The Petro-archaeometric Study of Glass-Making and -Working Indicators from the Ligurian Sites (S. L., B. M. and M. P. R.)	496
6.1.4 Conclusions	511
Acknowledgements	511
References	512
6.2 Venetian Soda Glass	515
6.2.1 Introduction	515
6.2.2 Analysed Samples	516
6.2.3 The Origins (Early Medieval Glass) and the Levantine Influence	518
6.2.3.1 The Transition from Natron to Soda–Plant-Ash Glass	518
6.2.3.2 Glassmaking and Glassworking	520
6.2.3.3 Venetian and Levantine Glass	522
6.2.4 Middle Ages and Renaissance	523
6.2.4.1 Venetian Glassmaking	523
6.2.4.2 Glass Analyses	524
6.2.4.3 Decolorisers	526
6.2.4.4 Common Glass, Vitrum Blanchum and Cristallo	527
6.2.5 Eighteenth Century: the Decline	530
6.2.6 Façon de Venise Glass	531
6.2.7 Other Glasses	531
6.2.8 Conclusion	532
References	533
6.3 Transfer of Glass Manufacturing Technology in the Sixteenth and Seventeenth Centuries from Southern to Northern Europe: Using Trace Element Patterns to Reveal the Spread from Venice via Antwerp to London	537
6.3.1 Introduction	537
6.3.1.1 Venice	537
6.3.1.2 Antwerp	538
6.3.1.3 Amsterdam	539
6.3.1.4 London	539
6.3.2 Background Information	540
6.3.2.1 Raw Materials	540
6.3.2.2 Venetian Glass Compositions	540
6.3.2.3 Published Façon-de-Venise Glass Compositions	541
6.3.3 Materials and Methods	541
6.3.3.1 Analysed Glass Samples	541
6.3.3.2 Techniques of Chemical Analysis	545
6.3.4 Results and Discussion	547
6.3.4.1 Compositional Groups among the Antwerp Soda-Glass Vessels	548
6.3.4.2 Comparison of the Composition of AC/VC and of the AVB/VVB Groups at the Trace Level	551

6.3.4.3	Major Composition of Façon-de-Venise Glass from Amsterdam	554
6.3.4.4	Major Composition of Façon-de-Venise Glass from London	555
6.3.4.5	Trace Element Patterns in Venetian Glass and in Façon-de-Venise Glass from Antwerp, Amsterdam and London	556
6.3.4.6	Sr-Nd Isotope Analysis of Antwerp FDV vs. VC and VVB Glass	558
6.3.5	Conclusions	559
	Acknowledgements	560
	References	560
6.4	Seventeenth-Century Varec Glass from the Great Hall of Mirrors at Versailles	563
6.4.1	Introduction	563
6.4.2	Experimental Determinations	565
6.4.3	Experimental Results	566
6.4.4	Analysis of the Results: What Came from Where?	567
6.4.5	Discussion	569
6.4.6	Conclusions	569
	Acknowledgements	571
	References	571
6.5	Seventeenth- and Eighteenth-Century English Lead Glass	573
6.5.1	Introduction	573
6.5.2	Historical Background	573
6.5.3	Previous Research	574
6.5.4	Objectives	575
6.5.5	Analytical Method	576
6.5.6	Study Results and Discussion	577
6.5.7	Manufacture and Weathering of Replica Glasses	580
6.5.8	Conclusions	581
	Acknowledgements	581
	References	581
7.1	Metal Nanoparticles in Glass: Lustre	583
7.1.1	Introduction	583
7.1.2	Historical Notes	585
7.1.3	Lustre Composition and Morphology	586
7.1.3.1	Nanoparticle Size and Distribution	586
7.1.3.2	Metallic and Oxidised Phases of Silver and Copper	589
7.1.3.3	In-Depth Chemical Distribution	593
7.1.4	Lustre Formation Process	594
7.1.4.1	Ancient Recipes	594
7.1.4.2	Ion-Exchange Mechanism	595
7.1.4.3	Nucleation and Growth of Nanoparticles	597
7.1.5	Optical Properties of Lustre	598
7.1.5.1	The Surface Plasmon Resonances	598
7.1.5.2	Metallic Reflections	600
7.1.5.3	The Dichroic Effect	601

7.1.6 Conclusion	604
References	604
7.2 Glass Degradation by Liquids and Atmospheric Agents	609
7.2.1 Introduction	609
7.2.1.1 Glass Structure	610
7.2.1.2 Effects of Weathering	612
7.2.2 The Corrosion of Glass	614
7.2.2.1 General Aspects and Theory	614
7.2.2.2 Analysis of Glass Corrosion	619
7.2.2.3 Influence of Glass Composition on the Corrosion of Glass	623
7.2.2.4 Influence of the Corrosion Medium	624
7.2.2.5 Simulation of the Glass Corrosion	625
7.2.3 The Weathering of Glass	626
7.2.3.1 General Aspects	626
7.2.3.2 The Influence of Humidity and Acidifying Gases	628
7.2.3.3 Chemical Composition of the Weathering Products	630
7.2.3.4 Deterioration Rate	634
7.2.3.5 Influence of Particulate Matter	638
7.2.3.6 Other Types of Glass Weathering	640
7.2.4 Summary and Conclusion	641
7.2.5 Acknowledgements	642
References	642
7.3 Corrosion of Stained Glass Windows: Applied Study of Spanish Monuments of Different Periods	653
7.3.1 Introduction	653
7.3.1.1 Previous Considerations	655
7.3.2 Mechanisms of Chemical Attack	655
7.3.3 Environmental Degradation Effects	656
7.3.3.1 Intermediate Decay Phenomena of Medieval Stained Glasses: The Presence of Carbonates	656
7.3.3.2 Complete Decay Phenomena of Medieval Stained Glasses: The Presence of Sulfates	659
7.3.3.3 Degradation in Renaissance Stained Glass Windows	662
7.3.3.4 Weathering Effects on Stained Glass Windows from the Nineteenth and Twentieth Centuries	665
7.3.3.5 Weathering of Decorations	667
7.3.3.6 Weathering of Other Components	671
7.3.4 Conclusions and Outlook	672
Acknowledgements	673
References	673
7.4 Novel Methods of Evaluation for the Conservation of Browned Historical Stained Glass	677
7.4.1 Introduction	677
7.4.2 Background	678
7.4.2.1 Glass Weathering and Mn-Browning	678

xviii *Contents*

7.4.2.2 Conservation Treatments for Mn-Browning	680
7.4.3 Corroded Glass Material	680
7.4.4 Methods of Analysis	682
7.4.5 Results Provided by the μ -XANES Measurements	683
7.4.6 Computed Tomography Monitoring of the Conservation Treatment	684
7.4.7 Conclusions	687
Acknowledgements	688
References	689
Index	691