THIN SECTION PETROGRAPHY GEOCHEMISTRY

& Scanning Electron Microscopy of

ARCHAEOLOGICAL CERAMICS

PATRICK SEAN QUINN

Archaeopress
Summertown Pavilion
18-24 Middle Way
Summertown
Oxford
OX2 7LG

wwww.archaeopress.com

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Cover images:

Front cover
Top row left to right: ceramic statue of Emperor Shihuang's terracotta army being analysed geochemically via portable X-ray fluorescence spectrometry; cross polarised thin section photomicrograph of Bronze Age pottery, Greece, with metamorphic inclusions; extract of raw geochemical dataset on archaeological ceramic sherds with minor and trace element values.

Bottom row left to right: cross polarised thin section photomicrograph of historic concrete, Scotland, with basalt aggregate particle; bivariate scatterplot of the abundance of the elements calcium (Ca) and cobalt (Co) in Bronze Age ceramic transport jars from Greece, labelled by typology, revealing a broad split in the dataset; back scattered scanning electron microscope image of polished cross section of Late Prehistoric pottery, California, USA.

Back cover
Top row left to right: plane polarised thin section photomicrograph of Anglo Saxon pottery, England, with bone temper; macrofabric of Inca pottery sherd seen in fresh break with low magnification reflected light microscope; false colour micrograph of mineralogical composition of Late Prehistoric pottery, California, USA, determined by scanning electron microanalysis.

Bottom row left to right: cross polarised thin section photomicrograph of Islamic fritware tile, India; scanning electron microscope with energy dispersive detector; cross polarised thin section photomicrograph of sand tempered Medieval pottery, England, with grain size distribution histogram of inclusions recorded by point counting.

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PREFACE

This book is dedicated to the scientific compositional analysis of ancient ceramics. It provides theoretical and practical guidelines for their study via the techniques of thin section petrography, instrumental geochemistry, scanning electron microscopy and X-ray diffraction.

With over 400 photomicrographs of prehistoric, historic and traditional ceramics from 50 countries worldwide, as well as raw material specimens, ethnographic and experimental samples, it can be used as a reference manual for the identification and interpretation of the compositional and microstructural phenomena that occur within ancient ceramics. The detailed accompanying text and logical chapter structure means that it may also serve as a course book for specialist training in ceramic compositional analysis, as well as for self-study.

The bulk of the book is dedicated to the versatile technique of ceramic petrography, detailing the main steps involved in the preparation of archaeological thin sections, their petrographic characterisation and classification, and their interpretation in terms of the provenance and technology of ceramics.

The book focuses mainly on utilitarian, coarse, earthenware and terracotta pottery, which dominate most ancient ceramic assemblages. However, the petrographic analysis of ceramic building materials, refractories and high-fired glazed ceramics such as porcelain and fritware, as well as cementitious materials, are covered in a separate dedicated chapter.

It is assumed that the reader has a basic knowledge of optical mineralogy and the thin section petrography of rocks. The book should therefore be used in conjunction with standard geological texts and identification guides dedicated to these topics.

The related technique of ceramic geochemistry is covered in detail in a dedicated chapter, which aims to provide a digestible introduction for beginners, as well as structured guidelines for more experienced researchers. This chapter details the geochemical composition of ancient ceramics and its relationship to their petrography, geological origins and technology. It takes readers through the steps involved in the geochemical study of ceramics, from the choice of technique and elements, through data quality assessment and the detection of elemental patterning via multivariate statistics, to the interpretation of these signals in terms of ceramic raw materials and provenance. An introduction to atoms, elements and the periodic table is provided, and mathematics, statistics and computer code have been kept to a minimum.

The application of scanning electron microscopy (SEM) and X-ray diffraction (XRD) are presented as supplementary methods of ceramic compositional analysis that can be used to address specific archaeological topics, particularly that of technological reconstruction.

The book has drawn upon the author's research, consultancy, teaching and supervision on archaeological ceramic analysis via thin section petrography, geochemistry, SEM and XRD. It also builds on an extensive accumulated body of knowledge on these topics. A further reading section at the end of each chapter. provides relevant studies that the reader can refer to for more detail on specific topics.

Given that few publications dedicated to the thin section petrographic, geochemical, SEM and XRD analysis of archaeological ceramics exist, and that these approaches are undertaken in a number of different ways, this book is likely to contain some views or interpretations that divide opinion. Attempts have been made to cover a range of alternative methods in addition to those of the author, where these are relevant to the topics being discussed.

Chapter 1

INTRODUCTION TO ARCHAEOLOGICAL CERAMICS & COMPOSITIONAL ANALYSIS

1.1 Archaeological Ceramics

Archaeological ceramics are clay or carbonate-rich composite inorganic artefacts that were produced and used by past humans. They include pottery (Fig. 1.1), figurines (Fig. 1.2), ceramic building materials (Fig. 1.3), refractories, clay writing tablets, clay smoking pipes, loom-weights, seals and a range of other clay objects, as well as cementitious objects and structures such as plaster, mortar and concrete. Ceramics represent some of the earliest synthetic materials that were intentionally created by humans. In many cases their production involved the use of high temperature 'pyrotechnology'. The discovery of the unique material properties of naturally occurring clay and the utilisation of these to create hard, semi-permanent objects of a desired shape was a crucial step in the development of ancient craft technology.

The widespread use of ceramics in ancient societies and their relatively slow degradation in the archaeological record makes them one of the commonest types of ancient artefact of many periods and geographic regions (Fig. 1.4). As such they represent a key resource with which to interpret the activities of past humans and reconstruct deeper aspects of their cultures. Archaeological applications of ceramics include the study of both mundane and ritual activities at ancient sites, the detection of trade, exchange and cultural interaction between social groups, the reconstruction of craft technology and the organisation of production. Ceramics can be used to speculate about deeper, less tangible aspects of past cultures such as their belief systems, their traditions and identities. They have also traditionally played a role in the dating of archaeological sites and can be used, with caution, to identify the existence of specific cultural groups.

In order to address the above topics, it is necessary to collect specific types of data from ancient ceramic assemblages and interpret this within their wider archaeological context, as well as an appropriate theoretical framework. Ceramics can be studied in many ways, by recording different characteristics, ranging from simple visual observations of their gross form and surface decoration (Fig. 1.5) to the scientific characterisation of their compositional signatures and microscopic structures using sophisticated analytical equipment (Section 1.2) (Fig. 1.6).

1.2 Ceramic Compositional Analysis

The detailed study of the clay- or carbonate-rich material that ancient ceramics are made of can be referred to as 'ceramic compositional analysis'. Clay is a naturally occurring substance that forms from the weathering of rock (Sections 3.2 & 5.2), and ceramic compositional analysis therefore draws upon the scientific study of rocks and sediments. It can be roughly subdivided into mineralogical, geochemical and microstructural approaches. These differ in terms of the apparatus used and the scale of analysis. Mineralogical techniques such as thin section petrography (Section 1.3; Chapters 2–7) and X-ray diffraction (XRD) (Section 9.6) are used to characterise

Fig. 1.1 Archaeological ceramics. Typical pottery vessels with a range of shapes and functions, recovered from a Bronze Age tomb at Jericho during the 1952–1958 excavations by the Institute of Archaeology, London.

Fig. 1.2 Life-size ceramic figurines. These reconstructed statues of Emperor Qin Shihuang's mausoleum near Xi'an, China, dated to the third century BC, are one of the world most renowned and fascinating ceramic finds.

Fig. 1.3 Ceramic building material. This brick is one of over 250,000 used to pave the floor on which the statues in Fig. 1.2 stood. Qin period, China.

Fig. 1.4 Ceramic sherds in situ in archaeological strata. Discarded broken pots represent one of the most common artefact types at many ancient sites. Neolithic Serbia.

Fig. 1.5 Pottery sherd being studied by eye. This comes from a coarse terracotta vessel and exhibits visual evidence for its method of manufacture in the form of wiping marks on the exterior surface. Bronze Age pottery, England.

Fig. 1.6 Dedicated scientific laboratory for the materials science analysis of archaeological ceramics, including SEM, LA-ICP-MS, XRD and X-radiography. Wolfson Laboratories, Institute of Archaeology, University College London.

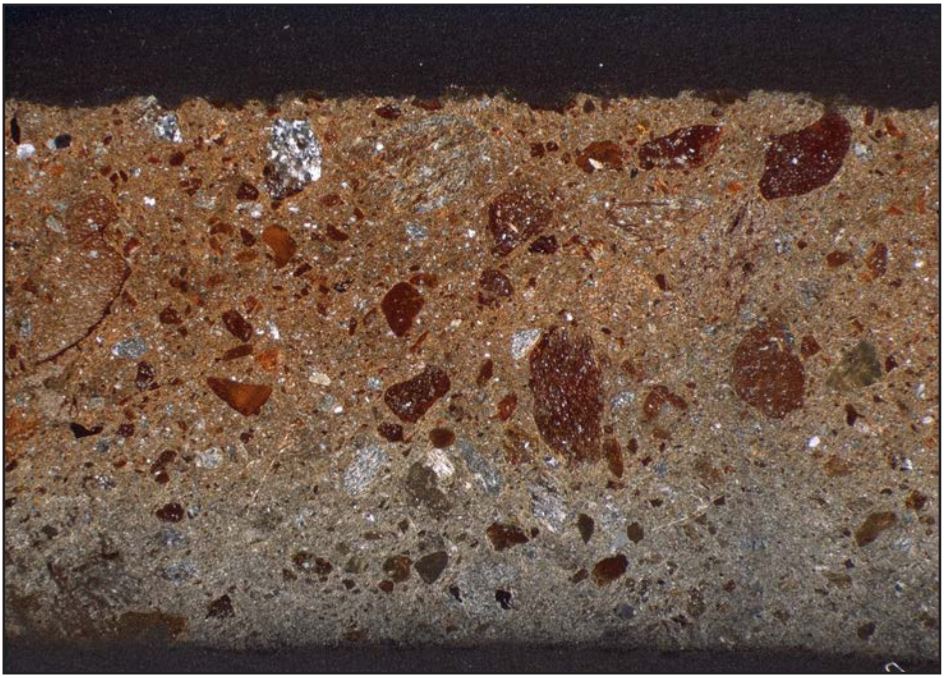
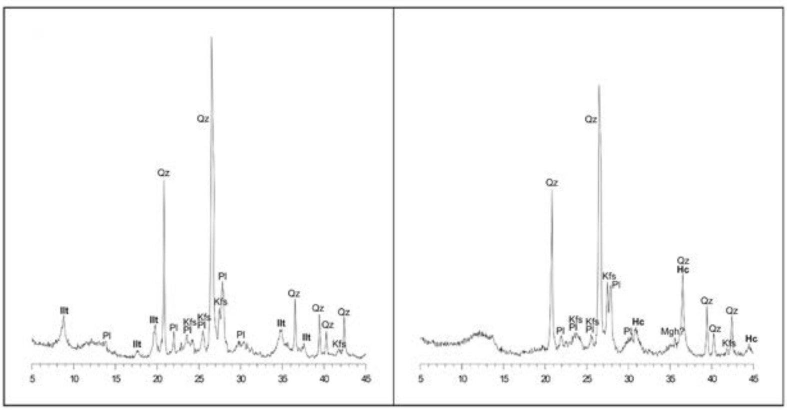


Fig. 1.7 Archaeological ceramic sherd seen in thin section under the polarising light microscope, revealing the presence of mineral and rock fragments derived from a metamorphic source. This means that it was likely to have been produced in a region where rocks of this type occur. Neolithic pottery, Greece. Image width = 14.0 mm.

Fig. 1.8 Diffractogram of the mineralogical composition of two archaeological ceramic sherds, as recorded by X-ray diffraction (XRD). The sample on the right was fired at a higher temperature due to the presence of hercynite (Hc) and the absence of illite (Ilt). Medieval pottery, Spain. From Travé Allepuz et al. (2014, fig. 9, p. 399)



archaeological ceramics in terms of the types of minerals that they contain (Figs. 1.7 & 1.8) and their abundances. In the case of thin section petrography, small grains or 'inclusions' of rock can be identified under the microscope using geological techniques (Fig. 1.7). X-ray diffraction uses the interaction of X-rays with the crystalline structure of the minerals in the ceramic specimen and can detect the presence of clay minerals as well as 'phases', formed at high temperature during firing (Fig. 1.8).

Geochemical techniques of ceramic compositional analysis such as instrumental neutron activation analysis (INAA), X-ray fluorescence spectroscopy (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) (Chapter 8) look beyond the mineral to the constituent atoms within a sample. They use various principles from the physical sciences (e.g. neutron bombardment, X-ray excitation, ionisation) to detect the types of atomic elements present and quantify their abundances (Fig. 1.9), down to the level of parts per trillion (0.0000000001%).

Scanning electron microscopy (SEM) (Sections 9.2–9.5) and thin section petrography can be used to investigate the microstructure of archaeological ceramics at high magnification (x50,000) and detect compositional features and particles that are way beyond the resolution of the human eye (Figs. 1.7 & 1.10). The arrangement of the mineral and rock inclusions, the clay 'matrix' and pores or 'voids' within ceramics are of key importance for the compositional study of ceramics. Microgeochemical data can also be obtained on the elemental composition of these individual phenomena using the SEM coupled with energy-dispersive X-ray spectroscopy (EDS) (Section 9.3).

Despite the different apparatus used and types of data collected, mineralogical, geochemical and microstructural techniques of ceramic compositional analysis share similar goals and theoretical assumptions, and they are therefore largely complimentary. They are used to characterise the composition of ceramic specimens (Sections 4.2.2, 4.3 & 8.2), detect patterning both within and between samples, and classify them into compositional groups of archaeological significance (Sections 4.2.1, 4.3.4 & 8.8) (Fig. 1.11). Numerical multivariate geochemical data is typically subjected to statistical procedures in order to explore its patterning (Fig. 1.12).

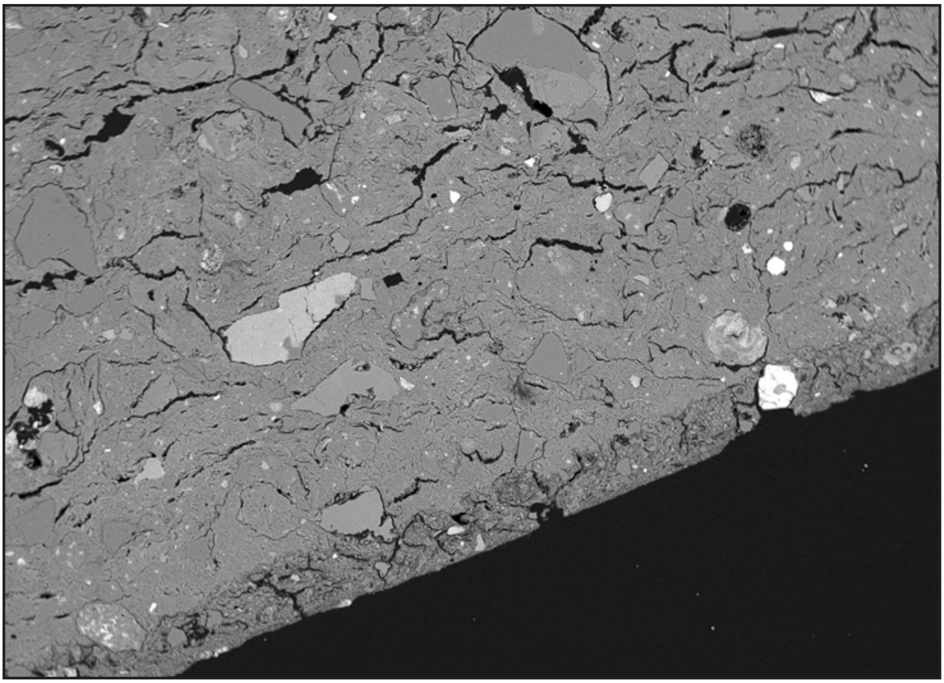
Compositional variability within archaeological ceramic assemblages often reflect the use of different types of raw materials and manufacturing techniques. By characterising the chemical and mineralogical composition of the raw materials of ancient sherds it is possible to interpret their geological characteristics (Sections 5.2, 8.2 & 8.10). As the composition of rock and clay varies from place to place, a comparison between ceramic composition and the nature of local and regional geology can be used to determine the production location or 'provenance' of ceramics (Chapter 5 & Section 8.11). Provenance studies are often supported by the collection of potential ceramic raw material sources in the field (Sections 5.4 & 8.11). Scientific provenance determination provides key evidence for the for movement of ceramics via processes such as trade and exchange, migration and settlement shift, which can be used to test assumptions based on the form and decoration of sherds (Fig. 1.13)

Whilst they are made from naturally-occurring materials, archaeological ceramics are synthetic objects, produced by past humans. Some ceramics were manufactured via a complex process that involved many different steps. Evidence for the production sequence or 'chaîne opératoire' of ceramics can be visible to the naked eye (Fig. 1.5) but also resides within the mineralogical, chemical and microstructural composition of sherds (Chapter 6; Sections 8.12, 9.2 & 9.6). The latter is particularly informative and can reveal the details of the clay 'paste' recipes (Section 6.3) (Fig. 1.14) and firing procedures (Sections 9.2 & 9.6) (Fig. 1.15) of ancient ceramics. The reconstruction of ceramic craft technology via methods such as thin section petrography, SEM and XRD provides important data with which to explore themes such as the traditions and

Sample	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	V	Cr	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Pb
1	0.54	23.88	71.15	0.72	0.30	1.04	0.01	1.71	90	270	28	35	29	25	28	48	50	155	23	116	41	82	18
2	0.69	24.21	69.65	1.32	0.27	1.07	0.01	2.44	128	261	30	16	28	26	59	62	43	167	21	163	34	79	21
3	0.41	19.74	74.86	0.45	0.30	1.05	0.01	2.74	111	260	27	34	32	22	17	38	43	196	22	100	30	77	75
4	0.66	28.22	65.96	1.14	0.36	1.15	0.01	2.10	102	264	32	14	39	30	50	68	54	191	27	174	47	98	27
5	0.58	24.92	69.96	0.60	0.31	1.13	0.01	1.83	92	297	31	20	29	28	23	49	52	171	25	124	38	83	17
6	0.69	25.19	68.42	1.19	0.28	1.09	0.01	2.70	88	267	33	14	41	26	55	62	46	187	24	190	48	89	24
7	0.64	23.91	66.37	1.71	0.39	1.12	0.01	5.19	101	179	33	23	60	27	75	116	46	217	28	460	43	97	29
8	0.58	20.65	74.35	0.76	0.29	1.03	0.01	1.97	129	254	27	29	33	23	32	44	45	189	23	117	43	85	18
9	0.33	19.65	76.62	0.27	0.32	1.02	0.01	1.37	75	242	25	18	28	20	8	32	48	177	19	73	37	71	12
10	0.79	20.88	71.93	0.68	0.31	1.03	0.01	2.66	115	278	36	23	27	24	28	46	47	188	21	113	41	88	19
11	0.43	19.01	76.13	0.54	0.37	0.76	0.01	2.17	61	239	24	41	35	19	21	44	33	167	13	141	32	28	21
12	0.55	15.97	77.42	1.23	0.40	0.74	0.01	2.97	106	138	29	35	47	15	44	46	36	304	19	195	28	36	22
13	0.54	20.68	74.72	0.70	0.30	0.61	0.01	2.10	70	301	46	53	38	15	30	39	27	146	15	114	30	27	17
14	0.59	21.36	72.96	1.23	0.36	1.00	0.01	2.01	104	303	26	15	35	21	52	61	39	201	21	202	43	57	31
15	0.71	15.71	78.28	0.86	0.36	0.73	0.02	2.86	99	225	27	108	32	19	26	39	29	175	16	155	22	27	15
16	0.58	22.40	70.64	0.95	0.40	1.24	0.01	3.11	165	261	33	35	37	32	51	62	48	241	26	262	39	48	30
17	0.50	25.63	65.62	1.43	0.77	1.34	0.01	3.47	154	230	34	26	53	34	72	104	45	209	30	461	29	40	36
18	0.86	22.44	69.59	1.00	0.40	1.21	0.02	3.24	131	229	32	29	33	27	54	55	45	245	31	197	26	41	28
19	0.69	23.25	69.58	1.78	0.41	1.19	0.01	2.66	146	336	23	15	31	29	87	82	38	263	41	267	40	56	39
20	0.41	22.67	69.33	1.11	0.50	1.32	0.01	3.01	173	214	34	35	43	32	56	99	48	320	52	396	27	46	36
21	0.57	19.45	75.53	0.28	0.32	0.92	0.01	1.44	74	263	28	19	22	17	9	34	45	248	57	66	34	88	15
22	0.26	19.21	77.08	0.26	0.29	0.94	0.02	1.48	65	295	31	32	25	19	10	34	45	268	66	65	24	85	17
23	0.39	19.36	76.05	0.47	0.28	0.77	0.01	2.11	56	239	23	22	49	18	15	39	30	153	15	134	36	44	18
24	0.31	19.09	76.96	0.30	0.32	0.92	0.02	1.58	87	267	21	53	22	19	9	34	50	161	19	85	47	109	13
25	0.78	22.20	70.78	0.97	0.26	0.98	0.01	2.47	115	288	27	20	35	24	45	53	40	180	18	166	44	77	26
26	0.47	15.78	80.25	0.54	0.36	0.71	0.01	1.53	78	263	18	32	21	17	20	41	25	161	12	124	22	24	16
27	1.16	16.79	77.23	1.36	0.09	0.71	0.02	1.58	78	226	18	69	43	18	24	20	26	144	14	102	28	32	15
28	0.55	16.57	79.24	0.87	0.17	0.72	0.01	1.53	117	242	18	27	58	20	23	29	25	151	14	113	24	31	15
29	0.51	17.54	78.30	0.85	0.21	0.73	0.01	1.49	59	237	18	34	71	19	15	30	25	153	16	107	28	32	14
30	0.48	17.41	78.36	0.62	0.32	0.72	0.01	1.70	82	211	18	44	62	18	18	37	25	153	13	120	29	27	16
31	1.04	18.32	74.52	1.74	0.46	0.79	0.01	2.79	124	267	31	20	81	20	75	62	30	156	16	208	48	82	24
32	0.93	25.59	65.81	1.37	0.41	1.03	0.02	4.35	106	281	35	16	43	25	65	78	68	221	22	214	161	389	54
33	1.08	23.40	66.85	1.60	0.40	1.00	0.01	4.00	164	287	35	23	40	25	73	80	60	222	22	246	144	340	55
34	0.82	23.87	68.39	1.37	0.37	0.98	0.01	3.71	184	282	33	15	39	22	64	74	60	210	18	221	132	336	48
35	0.84	26.11	65.33	1.37	0.39	1.07	0.01	4.34	198	237	37	18	42	25	64	75	68	219	23	212	151	383	53
36	0.77	22.38	71.01	1.19	0.34	1.00	0.01	2.86	115	283	35	48	54	24	55	54	47	269	20	186	46	96	28
37	0.68	24.20	69.32	1.11	0.36	1.20	0.01	2.68	118	280	23	32	43	27	48	62	38	224	22	193	50	105	31
38	0.66	19.36	75.42	0.76	0.26	0.76	0.01	2.36	109	261	32	32	53	20	38	42	40	202	18	158	36	58	23
39	0.46	18.20	76.01	0.45	0.33	0.83	0.01	3.09	96	238	27	45	27	22	19	37	33	179	20	211	23	35	18
40	0.60	20.68	73.35	0.63	0.41	0.96	0.01	2.98	122	256	25	33	49	19	31	48	48	212	21	164	71	186	27
41	0.91	19.79	73.35	1.70	0.33	0.84	0.01	2.53	146	270	35	32	54	18	72	60	48	259	17	254	71	150	28
42	0.94	17.52	76.04	0.96	0.27	0.60	0.01	2.07	54	240	23	30	37	13	37	50	29	249	16	203	30	34	22
43	0.63	18.11	72.82	0.73	0.58	0.95	0.19	4.24	110	172	44	31	104	19	29	109	52	313	18	377	51	97	30
44	0.88	18.14	73.89	1.93	0.28	0.93	0.02	3.32	139	227	32	20	48	18	68	56	47	425	22	265	57	80	20
45	1.18	17.35	75.09	1.55	0.24	0.85	0.01	2.26	133	271	25	25	35	19	65	61	42	354	22	243	51	108	24
46	0.61	19.36	74.83	0.96	0.36	0.86	0.02	2.32	89	268	24	22	42	20	43	56	37	256	18	234	29	57	46
47	0.55	23.03	68.76	0.51	0.71	1.01	0.02	3.35	175	208	28	30	70	25	16	108	41	245	23	206	26	48	29
48	1.01	16.13	76.48	1.98	0.33	0.80	0.01	2.76	97	292	39	20	82	15	77	56	51	329	16	268	52	100	35
49	0.87	19.51	72.40	1.49	0.33	1.30	0.03	3.47	177	342	23	22	44	25	61	56	36	208	22	256	32	44	71
50	0.84	18.30	75.05	1.30	0.24	0.96	0.01	2.80	80	220	27	29	45	21	53	66	45	292	22	230	55	96	45

Fig. 1.9 Geochemical data on the abundance of 23 elements in 50 archaeological ceramic sherds, as recorded by X-ray fluorescence spectroscopy (XRF). Roman pottery, England. Data from Amicone and Quinn (2015).

Fig. 1.10 Archaeological ceramic sherd seen in polished cross section with the scanning electron microscope (SEM) in backscattered electron mode (BSE). This reveals numerous inclusions and elongate voids, as well as a thin decorative layer on the margin. Pre-Columbian pottery, Panama. Image width = 2.0 mm.



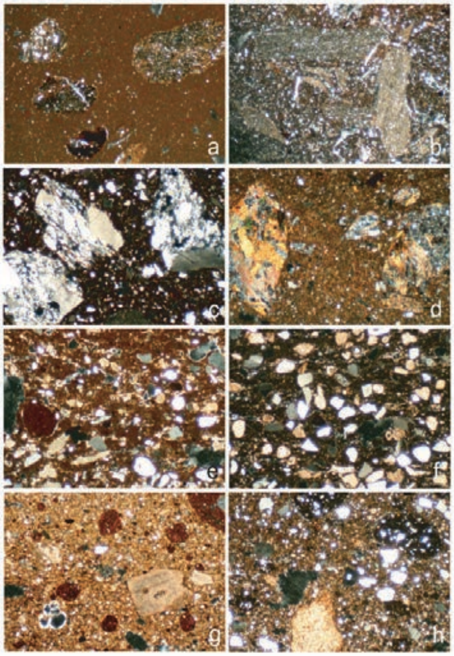
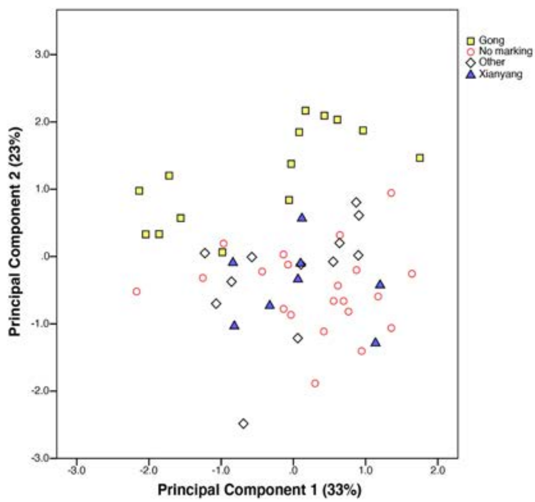


Fig. 1.11 Compositional patterning within archaeological ceramics from a single site, as seen in thin section. The images represent representatives of different 'fabrics' detected in this assemblage. Bronze Age pottery, Greece. Image width = 2.0 mm. From Day et al. (2011, fig. 4, p. 525).

Fig. 1.12 Statistical exploration of geochemical data on nine elements collected on 56 ceramic artefacts of the type in Fig. 1.2. The two dimensional distribution of the samples indicates a clear chemical difference between the 'Gong' and the other statue types. Qin Period, China. From Quinn et al. (2020, fig. 5c, p. 8).



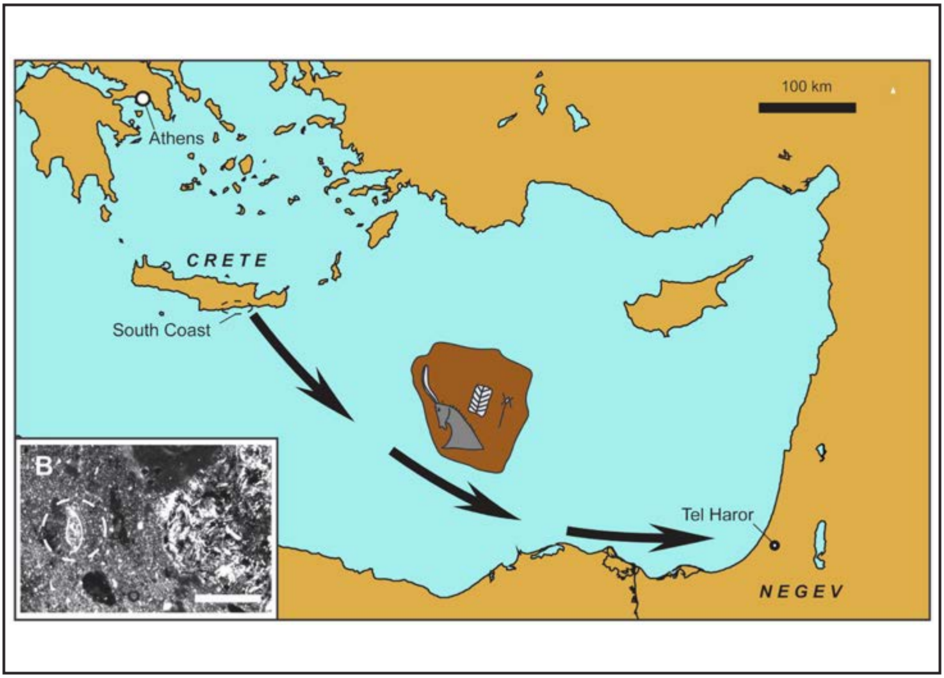
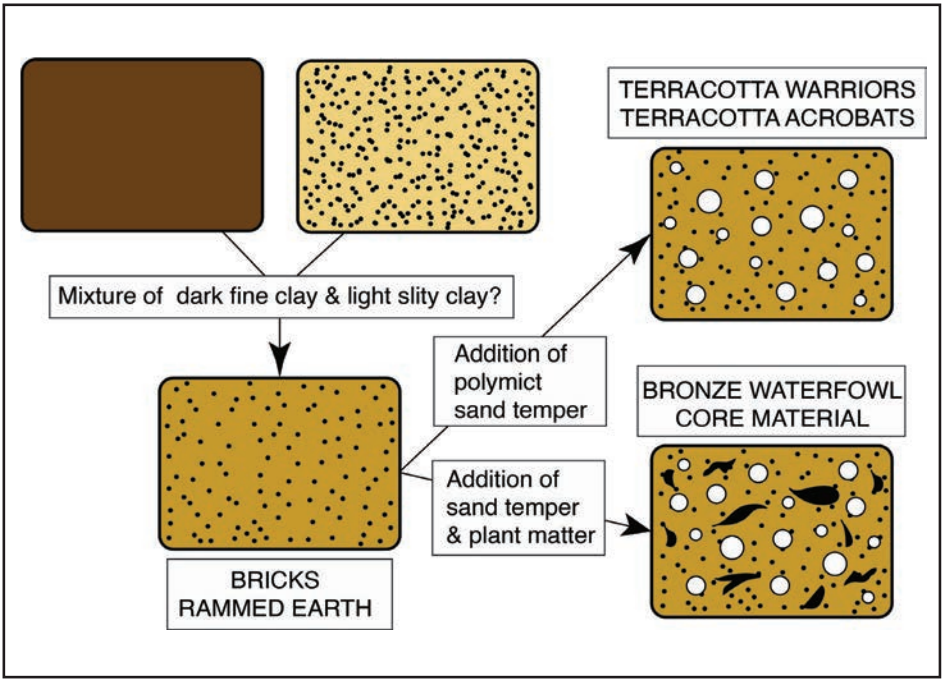


Fig. 1.13 Ceramic provenance determination. The composition of the pictured sherd is incompatible with its find spot in Israel. It has a Minoan inscription suggesting that it came from Crete. It's composition matches the geology and other Bronze Age ceramics from the south east coast of the island, which also contain rounded basalt inclusions (inset).

Fig. 1.14 Reconstructed paste preparation technology for the production of multiple ceramic types at Emperor Qin Shihuang's mausoleum near Xi'an, China (Fig. 1.2), based on thin section petrographic analysis. From Quinn et al. (2017, fig. 6, p. 974).



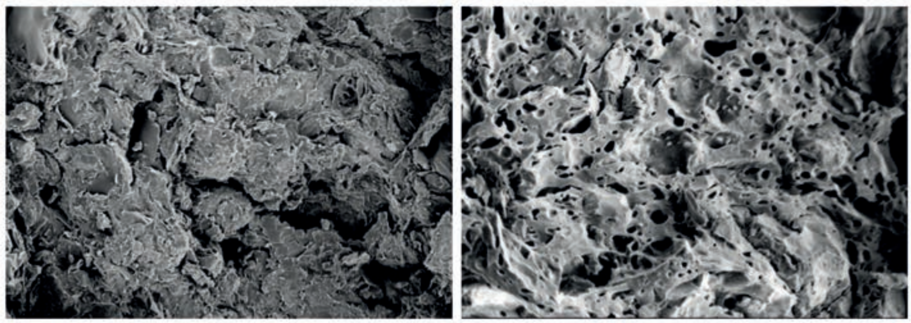


Fig. 1.15 Clay vitrification microstructure of archaeological ceramic sherds in the SEM. The sample on the left exhibits a rough appearance from the presence of the clay minerals, whereas on the right these have vitrified to form a glassy network. Neolithic pottery, Serbia. Image width = 0.1 mm (L) and 0.05 mm (R). Modified from Amicone et al. (2020, fig. 6).

Fig. 1.16 Simple, inexpensive polarising light microscope being used to examine an archaeological ceramic thin section. Despite its simplicity, detailed compositional analysis may be performed on such a microscope by a trained analysts.

identities of past people as well as their skill and capacity to innovate. Such investigations draw upon ethnographic studies of traditional ceramic production (Section 6.1) as well as experimental archaeology (Section 9.2). Ceramic technology also plays an important role in the investigation of how production was organised in past societies, including topics such as scale of production, standardisation and specialisation.

Scientific ceramic analysis is best applied in conjunction with evidence from traditional archaeological approaches to artefacts, such as their macroscopic study (Section 4.4). Compositional data should be used to answer specific questions and test hypotheses posed by these methods (Section 5.7; Figs. 1.12 & 1.13). The results of scientific investigation are most useful when they are considered within their wider archaeological context.

Ceramic compositonal analysis is used in the field of artefact conservation to determine the raw materials and recipes of objects and design strategies for their conservation and repair. It also plays a minor role in authentication and the detection of forgeries.

Many methods of ceramic compositional analysis are invasive in that they require the removal of a sub-sample of the object under study, which is then prepared in an appropriate format (Sections 2.3 & 8.3). This means that not all artefacts can be studied scientifically and some conflict exists between the needs of ceramic analysts and the role of museums and collections in preserving excavated specimens. Some methods are costly and make use of highly expensive equipment (Fig.1.6) that exists in only a small number of places (Section 8.3), which further limits the numbers of samples that can be analysed. Nevertheless, detailed compositional analysis can also be carried out using rather modest apparatus (Fig. 1.16), given sufficient expertise, and methods of non-invasive testing are starting to see widespread use within the field (Fig. 1.17), offering new opportunities for rapid analysis without the need to destroy irreplaceable artefacts.

Ceramics have been studied in detail ever since the development of the earliest scientific apparatus, such as the petrographic microscope in the mid 19th century. However, it was not until the latter half of the 20th century that ceramic compositional analysis became popular, with the rise of processual archaeology. It is now a well-recognised branch of 'archaeometry' that is undertaken by scientifically trained archaeologists as well as through collaborations with geologists, physicists and chemists. The field is diverse and contains multiple key laboratories and research groups on most continents, as well as specialist training courses for students and dedicated international and regional meetings and journals, through which findings are disseminated. While the subject relies on several well-established scientific methods, it also stays abreast of new technological innovations and incorporates these into its remit, where they are useful (Section 9.4).

Thin section petrography and bulk geochemistry are the two methods most commonly applied to the analysis of low fired earthenware and terracotta ceramics, which dominate most archaeological assemblages, as well as cementitious artefacts. Thin section petrography is introduced further in Section 1.3 below and explained in detail in Chapters 2–7. A dedicated guide to the principles and practice of the 'bulk' geochemistry of the clay body of ceramics is given in Chapter 8. The use of SEM for the microstructural and 'microgeochemical' analysis of archaeological ceramics is detailed in Chapter 9, followed by an introduction to the mineralogical analysis of ceramics via XRD. Several other techniques for ceramic compositional analysis exist, such as inductively coupled plasma mass spectrometry (LA-ICP-MS), Raman spectroscopy and synchrotron radiation.

Fig. 1.17 Archaeological ceramic sherd being non-invasively geochemically characterised via portable X-ray fluorescence spectroscopy (pXRF). The sherd has been placed within a lead-lined chamber (open for illustrative purposes) over the beam and detector of the instrument, and data is being recorded on a laptop. Roman pottery, England.

Fig. 1.18 Archaeological ceramic thin sections. These thin sections of pottery and cementitious ceramics (centre) have been produced with 76 x 26 mm (left) and 46 x 26 mm (right), as well as larger 76 x 46 mm (centre) glass slides. The section on the right has been carbon coated for study in the scanning electron microscope.

1.3 Introduction to Thin Section Petrography

Thin section petrography is the oldest scientific method used for the compositional analysis of archaeological ceramics. It however remains one of the most popular due to the rather simple level of technological investment required (Fig. 1.16), compared to geochemistry, SEM and XRD, as well as its versatile nature. It relies less on instrumental determination and instead requires more experience on the part of the analyst to identify features, characterise, classify and interpret the meaning of compositional signals within ceramics. For this reason, the following six chapters are dedicated to the subject of thin section petrography and outline in detail its principles, as well as providing a guide to the range of compositional phenomena that occur in ceramics under the microscope.

Ceramic thin sections are 30 µm thick slices of an artefact, fixed onto a glass microscope slide (Fig. 1.18) (Section 2.3). They are used in the geological disciplines of optical mineralogy and thin section petrography to analyse and classify rocks and minerals. Thin sections are studied at magnifications of x25–400 with a 'polarising' or 'petrographic light microscope' (Fig. 1.16). This uses two types of light: plane polarised light (PPL) (Fig. 1.19), which looks similar to regular transmitted light, and crossed polars (XP) (Fig. 1.20), in which the light is polarised in two directions and interacts with the mineral specimens in the thin section, producing optical effects that can be used for their identification.

Ceramic petrography applies the techniques of optical mineralogy and thin section petrography to archaeological material in order to identify the types of mineral and rock inclusions that they contain (Figs. 1.7, 1.19 & 1.20) (Section 3.3). Naturally occurring clay is a form of 'argillaceous' material and thus archaeological ceramics share certain characteristics with fine-grained clastic sediments. Ceramic petrography incorporates methodology from sedimentology and sedimentary petrography, such as the description of particle shape and texture (Sections 4.2.2.2 & 4.3.1). The abundant clay minerals within the clay matrix of archaeological ceramics (Figs. 1.19 & 1.20) (Section 3.2) are too small to be studied individually in thin section. Instead, ceramic petrography draws upon principles from the microscopic study of soils or 'soil micromorphology' to describe the nature of the matrix as well as the pores or 'voids' that occur in ceramic artefacts (Figs. 1.19 & 1.20) (Sections 3.4, 4.2.2.3 & 4.2.2.4).

Provenance determination may be carried out in thin section by identifying the mineral and rock inclusions in ceramics and relating these to geological maps or field samples of possible raw materials from their excavation location or other suspected sources (Chapter 5) (Figs. 1.7 & 1.13). In this respect it is much more suited to the detection of trade, exchange and other means of ceramic distribution than geochemistry (Section 8.11), at least for coarse ware sherds.

As synthetic artefacts, ceramics contain evidence of the technology involved in their manufacture (Chapter 6), including raw material processing, paste preparation (Figs. 1.14 & 1.21), forming, finishing and firing, as well as their use (Fig. 1.22). This is an important distinction that sets ceramic petrography apart from the microscopic study of natural earthy materials such as minerals, rocks, sediments and soil. A key aspect of the approach is therefore an appreciation of the craft of ceramic manufacture. This is normally provided by ethnographic studies of traditional pottery production, historical records and basic knowledge from materials science. Experimental archaeology is also used to investigate the effects of specific manufacturing techniques on natural raw materials, and is an integral part of ceramic petrography.

Ceramic petrography is most frequently performed on relatively coarse, low-

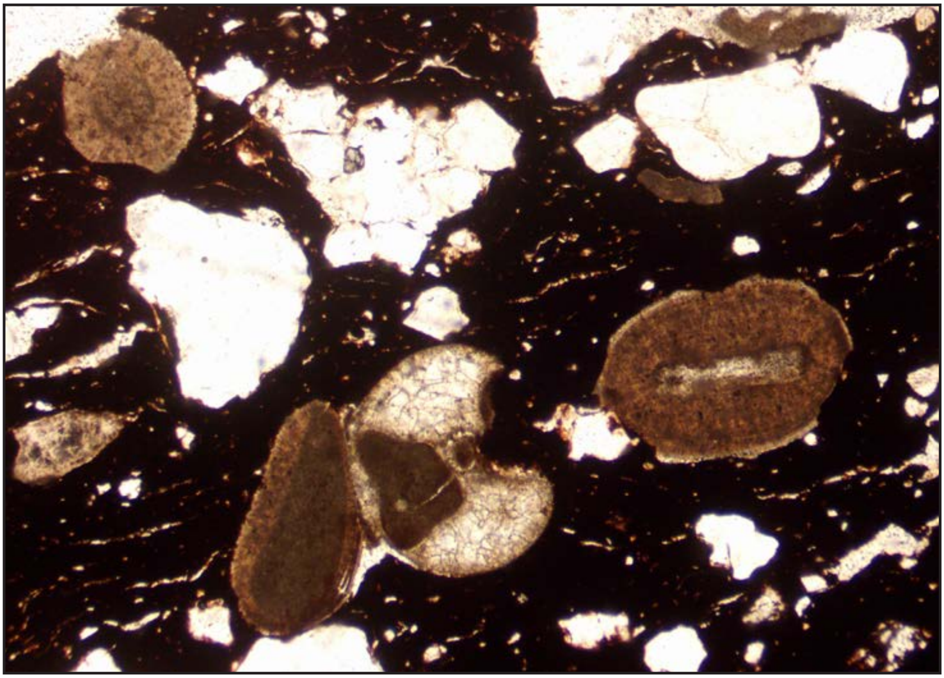
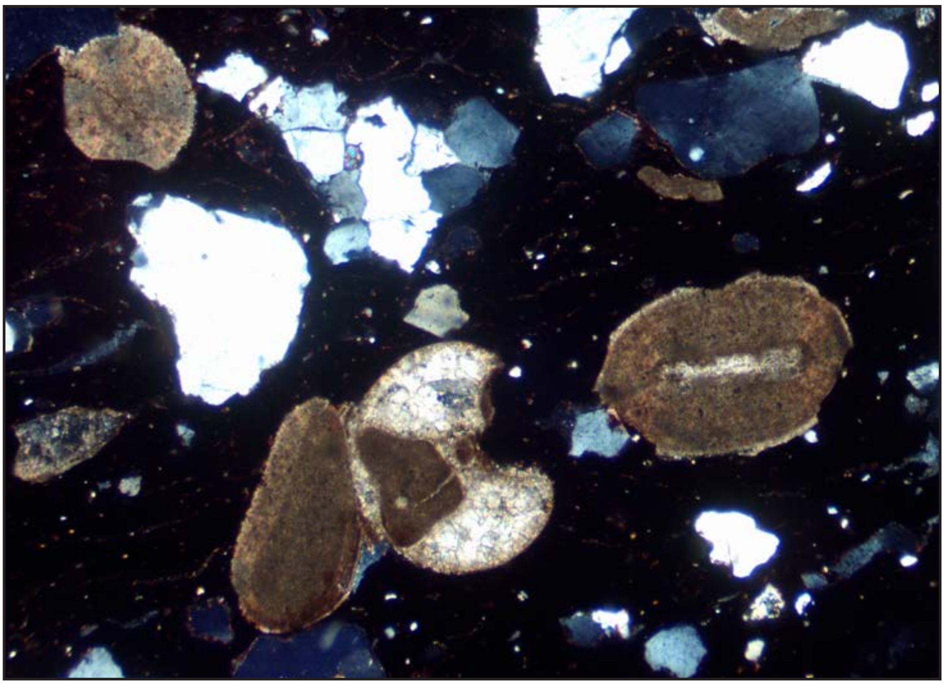


Fig. 1.19 An archaeological ceramic thin section seen at high magnification under the light microscope in plane polarised light (PPL). The dark brown is the clay matrix, which surrounds the white and light brown inclusions, as well as the white elongate voids. Compare with Fig. 1.20 below. Anglo-Saxon pottery, England. Image width = 2.9 mm.

Fig. 1.20 The same sample as Fig. 1.19 above, but seen in crossed polars (XP). The inclusion just above the centre is sandstone, made of quartz clasts and the one below it is oolitic limestone. The elongate voids appear black in XP. Anglo-Saxon pottery, England. Image width = 2.9 mm.



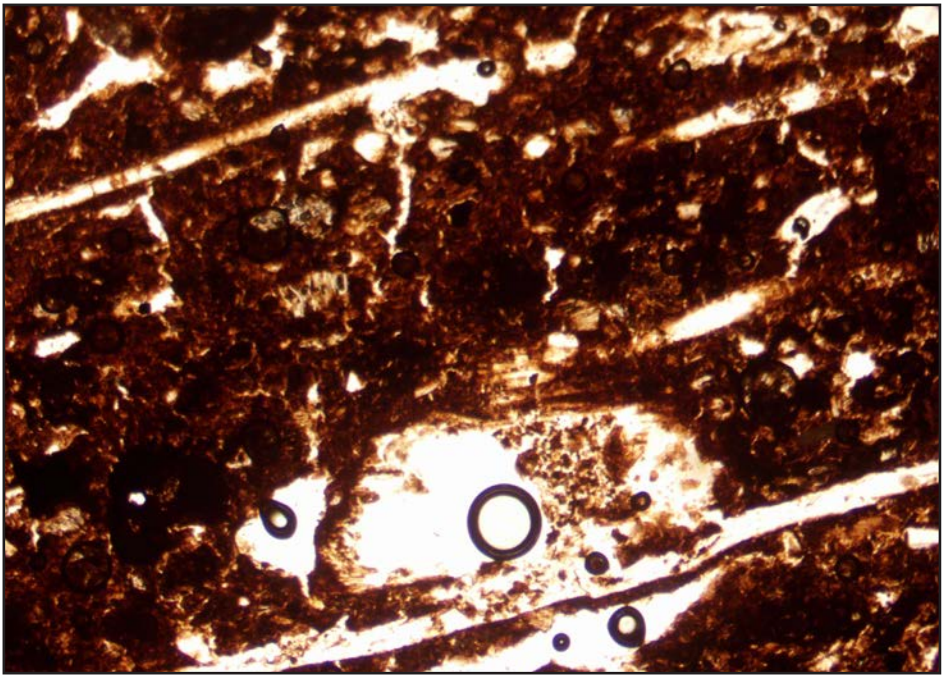
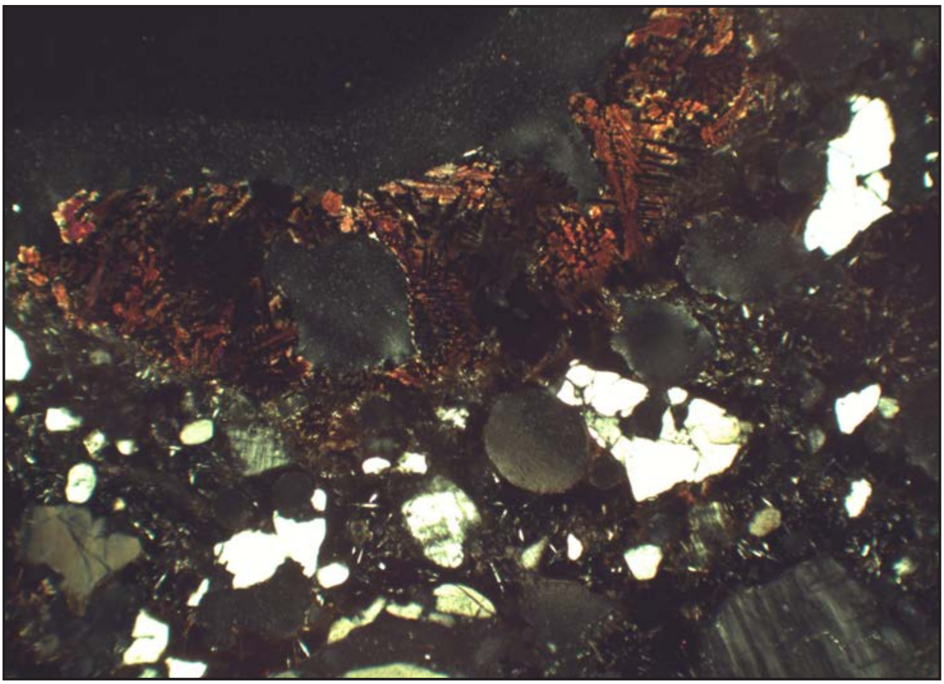


Fig. 1.21 Archaeological ceramic sherd with plant matter added to its paste. The elongate parallel sided voids in this sample were left from the combustion during firing of plant 'temper' that may have been added to modify the properties of the paste during forming. Medieval pottery, Ethiopia. PPL. Image width = 2.9 mm.

Fig. 1.22 Used ancient refractory ceramic in thin section. A layer of copper slag with a dendritic crystal structure is present on the margin, which grades into the vitrified ceramic body. Bronze Age smelting crucible, England. XP. Image width = 2.9 mm.



fired, utilitarian pottery vessels such as earthenware and terracotta, which tend to dominate ceramic assemblages, especially in prehistoric contexts. These are well suited to analysis in thin section due to their abundant inclusions. However, ceramic petrography can provide important insights into fine wares and higher fired glassy pottery types such as stoneware, fritware (Fig. 1.23) and sometimes porcelain (Section 7.7).

A wide range of non-pottery ceramic artefacts are also studied in thin section, including bricks and tiles (Section 7.2), clay crucibles and other refractories for metal and glass production (Section 7.4) (Fig. 1.22), as well as clay smoking pipes, loom-weights, seals, stamps and clay writing tablets (Section 7.5). The petrographic analysis of ancient cementitious building materials including plaster, render, mortar and concrete (Fig. 1.24) (Section 7.5) is closely related to that of archaeological ceramics and falls within the general remit of ceramic petrography. These are composed of calcareous 'binder' instead of clay and the intentionally added inclusions are referred to as 'aggregate'. Modern plaster and concrete are also analysed in thin section within engineering materials science (Fig. 1.24).

Ceramic petrography is mostly used to examine the composition of the main body or paste of ceramic artefacts. However, thin sections can also provide important information about the nature of finishing layers, such as slip, paint and glaze (Fig. 1.23) (Section 6.5), as well as deterioration effects and external deposits (Section 6.9).

Ceramic petrography can be used on its own as a research tool for interrogating aspects of the composition, technology and provenance of ancient artefacts. However, it works best when combined with data from the traditional macroscopic study of ceramics (Fig. 1.13) and other analytical techniques such as geochemistry, SEM and XRD in what has been referred to as an 'integrated' approach.

There is some debate over the correct name for the technique of analysing archaeological ceramics in thin section. The terms 'ceramic petrography' and 'ceramic petrology' are both widely used, sometimes interchangeably, and may therefore be considered as synonyms. In geology, the name petrography refers more specifically to the description and classification of rocks under the microscope, whereas petrology encompasses all aspects of their study. However, as archaeological ceramics usually contain abundant isolated mineral inclusions as well as fragments of rock (Figs. 1.7, 1.19 & 1.20) (Section 3.3), neither term fully describes their study in thin section. Furthermore, low-fired ceramics are composed of abundant clay minerals that are too small to be seen individually in the polarisng microscope (Section 3.2) and cannot therefore be studied via optical mineralogy. In this respect a more general term such as 'ceramic thin section analysis' might be more appropriate. Other labels given to the approach include 'mineralogical analysis' and 'optical microscopy' (OM).

The number of different names given to ceramic petrography is matched by similar diversity in the methods by which the technique is carried out. This is perhaps a consequence of its interdisciplinary nature and a strong reliance on approaches from the earth and environmental sciences, which are sometimes applied to ceramics without sufficient modification. Archaeologists, geologists and engineering material scientists independently undertake petrographic analysis of ancient ceramics, each guided by their own experience, standpoints and biases. Nevertheless, rigorous methodology for the qualitative description (Section 4.2.2) and quantitative characterisation (Section 4.3) of archaeological ceramics in thin section have existed for some years.

An advantage of thin section petrography, which sets it apart from geochemical approaches to compositional analysis (Chapter 8), is its ability to investigate both the provenance and technology of ancient ceramics. As a mainly visual approach (Section 4.2) it is highly flexible and can be modified to the material under study. The wide range of compositional phenomena that can occur in archaeological ceramics (Chapter 3) in thin

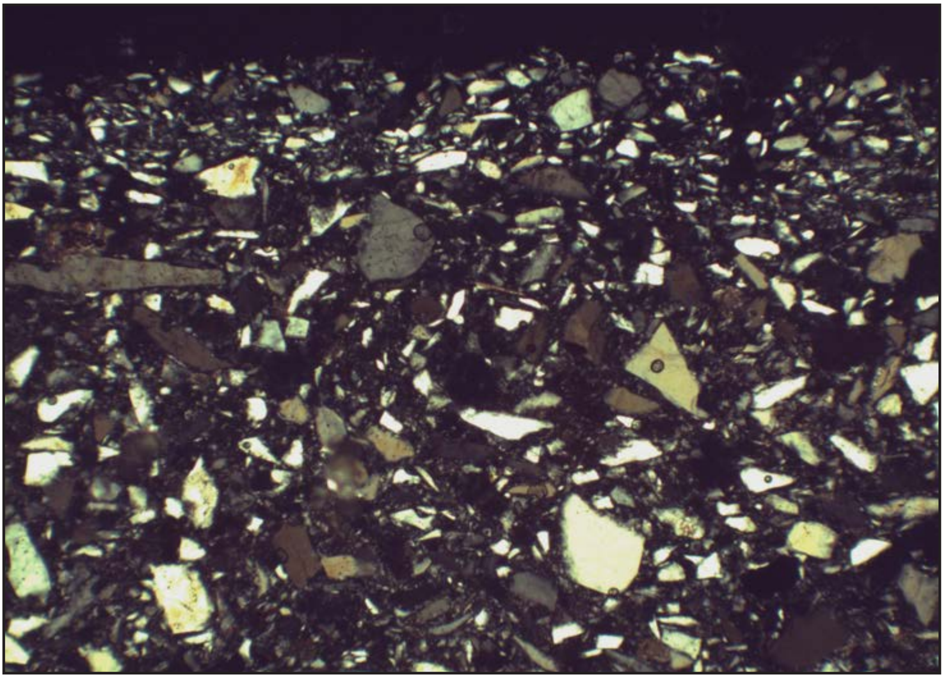
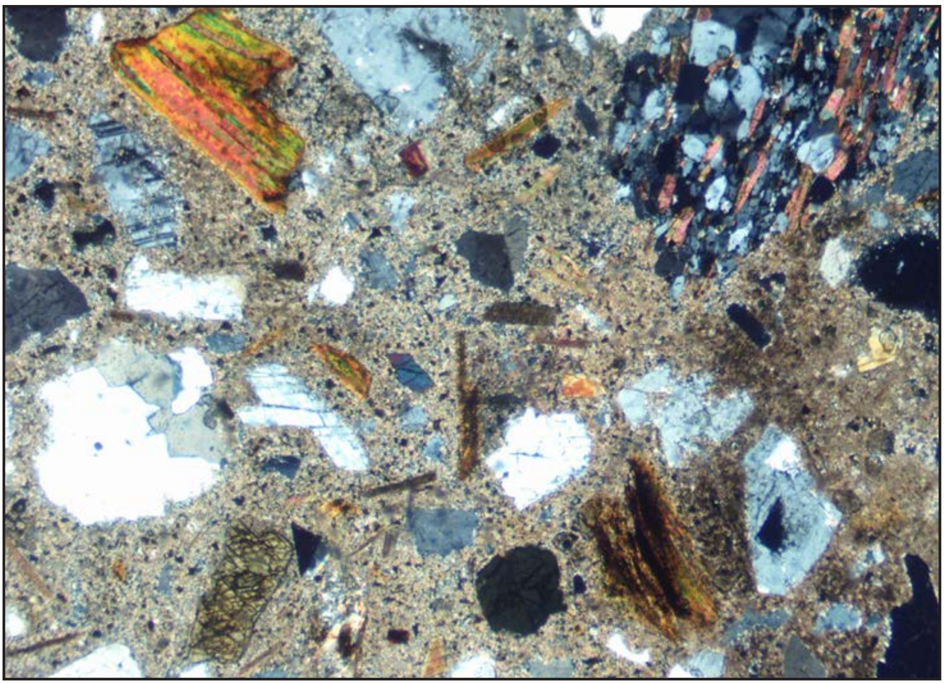


Fig. 1.23 Fritware/stonepaste ceramic artefact in thin section composed of angular, crushed quartz inclusions set in a glassy, isotropic matrix with abundant voids. The sample has a fritted glaze applied to the exterior. Islamic pottery, Turkmenistan. XP. Image width =2.9 mm.

Fig. 1.24 Photomicrograph of cementitious material in thin section. This is composed of a re-carbonated Portland cement 'binder' with angular aggregate deriving from igneous and metamorphic rock. 20th Century concrete, California, USA. XP. Image width = 2.9 mm.



section means that the fundamentals of the technique can take time to grasp, and experience is gained by exposure to material made in multiple regions with different geological raw materials and technology. Aspects of the method are somewhat subjective and therefore seem more like a 'art' than a science. Nevertheless, ceramic thin sections can also be studied via a strictly quantitative approach that focuses mainly on the inclusions but offers more objectivity (Section 4.3).

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