Applications of XRD analysis in Australian archaeological contexts: introducing the Olympus TERRA portable XRD analyser

Alice Mora

Abstract

X-ray diffraction (XRD) analysis is routinely applied to identify the crystalline phases of a wide range of geological, archaeological, and faunal materials. In recent years, industries have focused on the development of XRD instruments that are increasingly transportable, cost- and time-effective. The quality of data output of portable XRDs is becoming comparable to that of the conventional benchtop XRD systems.

The Olympus TERRA portable XRD analyser features a small vibrating sample holder that requires negligible sample amounts (10–15 mg) in powder form. It is lightweight, battery-operated and can be connected to personal devices via wireless connectivity. Reliable results can be achieved in a short timeframe (5–15 mins). Materials can be quickly analysed on-site with minimal sample destruction. These characteristics make this portable XRD a powerful tool for characterising, identifying and sourcing materials from Australian archaeological contexts.

Introduction

X-ray diffraction (XRD) analysis has proven to be a powerful tool in archaeological studies. This technique is successfully applied to characterise unknown materials and helps archaeologists in reconstructing past human behaviours. Unfortunately, the traditional benchtop XRD systems require a 'significant' amount of material in powder form, extended scanning times and a good level of expertise. These make the application of XRD analysis to archaeological materials challenging, especially in the Australian context, where quarantine regulations and ethical codes of conduct are (for good reasons) in place.

In recent years, industries have developed portable XRD instruments that require minimal sample size, are comfortably transportable, and able to generate inexpensive, quick and reliable data. Among the several portable XRDs available on the market, the Department of Archaeology and History at La Trobe University has recently acquired the Olympus TERRA portable XRD analyser, whose favourable characteristics will be highlighted in this short paper. The potential applications of XRD analysis in routine archaeological investigations across the Australian landscape will be discussed thereafter, and they include studies aiming to reconstruct past procurement and processing of raw materials, identifying if and how a material may have been heated, or assessing diagenetic alteration of faunal remains.

Department of Archaeology and History,
La Trobe University, Bundoora, Vic. 3086

A.Mora@latrobe.edu.au

X-ray diffraction analysis

X-ray powder diffraction analysis is routinely applied to a wide spectrum of geological, archaeological, and faunal materials to identify their constituent crystalline phases (minerals), the presence of amorphous components (e.g. glasses), and the determination of their respective amounts. The rationale behind this technique is that a crystal presents a structure characterised by a distinctive three-dimensional periodic array of atoms, which can diffract X-rays. When the X-rays are focused onto the crystalline phases, they are scattered by the constituting atoms at specific diffraction angles, depending on the periodic nature of a crystalline structure, i.e. the distance between its constituting crystallographic planes (d-spacing). The scattered radiation is collected by a detector, processed, and displayed in a diffractogram. The position, intensity and shape of the diffraction peaks act as a fingerprint for identifying a specific crystal structure (Pecharsky and Zavalij 2005). Therefore, XRD analysis can distinguish between materials that are chemically identical because of the distinctive ordered arrangements of their atoms. A common example is the three distinct forms of silica (SiO_2): glass (amorphous), quartz and cristobalite (both crystalline); which are distinguishable through their diffraction patterns (Smith 1998).

The Olympus TERRA portable XRD analyser

Traditional X-ray diffraction systems have a complex and extensive setup, and their use requires a high level of expertise. In recent years, industries have focused on the development of XRD instruments that are increasingly transportable, can be operated after quick training, leading to less costly and time-consuming analyses (Nakai and Abe 2012). The quality of data output of these new portable XRDs is competitive with, if not comparable to that of the conventional benchtop XRD systems.

Among the several companies that have developed portable versions of XRDs, Olympus has placed into the market a very successful product: the 'Olympus TERRA portable XRD analyser' (**Figure 1**). This instrument is very light, weighing around 15 kg with four batteries. It is safely contained in a sturdy box and can be transported on-site within its trolley, making it ideal for use during geological and archaeological fieldwork, as well as in museum and quarantine-regulated collections. This instrument is battery-operated (each set of batteries lasts around 4 hours) and it has wireless connectivity to personal devices (either laptop, smartphone or tablet). The measurement is visualised in real time on the personal device and the output data can be subsequently downloaded. The sample preparation is quick and easy; samples are reduced in particles smaller than 150 µm (100 mesh screen) using the crushing and sieving tools included in the set. The Olympus TERRA pXRD analyser requires only 10-15 mg of sample to run reliable measurements, making the analysis minimally destructive (and feasible in contexts that it would not normally be). Either bulk or selective sampling can be undertaken, including longitudinal and micro-area sampling.

Figure 1. The Olympus TERRA portable XRD analyser and the 'shaker'

Conventional XRD setups present a mobile configuration in which the components rotate relative to each other thanks to a goniometer, following Bragg-Brentano geometry. The sample (~ 300 mg) is grounded into a fine powder (<10 µm), homogenised, and appropriately pressed into the sample holder in order to avoid orientation effects. In contrast, in the Olympus TERRA portable XRD, the powder sample is inserted into one of the two sample chambers without any specific preparation thanks to the 'shaker'. This vibrating sample holder ensures that the crystals are randomly oriented by endless grain circulation. The new feature is possible because of the novel transmission geometry, which has first been developed in response to the challenging working conditions of the Mars Curiosity Rover and the limited dimensions of its XRD analyser (CheMin) (Downs and MSL Science Team 2015). In this type of configuration, the components are in a fixed position: the X-rays leave the tube (Cu or Co target), pass through a collimator, and collide into the sample, where they are diffracted by the array of grains onto a Charge-Coupled Device (CCD) detector. This allows the creation of an instrument of limited dimensions, easily transportable, which requires only minimal maintenance. Since the CCD camera can collect both diffraction and fluorescence data, the Olympus TERRA pXRD is at the same time an X-ray diffractometer and X-ray spectrometer (with an XRF energy range of 2.5 to 25 keV).

Another significant advantage is that the complete diffraction pattern of the sample is collected and displayed simultaneously (over the entire angular range of 5° to 55°) after the first exposure (~ 20 sec). In addition, the fluorescence data from the same sample is concurrently visualised in an XRF spectrum. This is adequate to quickly screen samples, such as understanding whether a known crystalline phase is present in the material, or to discriminate between two possible phases. Reliable data output can be achieved in less than 15 minutes, after approximately 50 exposures. More exposures will sharpen the diffraction peaks and reduce the background noise (**Figure 2**). The XRD data produced by the Olympus TERRA portable XRD analyser can be treated using two software packages: XPowder Software for Qualitative and Semi-Quantitative analysis, and Siroquant Software for Quantitative Rietveld analysis.

When using a conventional benchtop XRD, it takes around 10 minutes to quickly acquire the complete diffraction pattern because the sample is scanned at every possible angle. The resulting diffractogram will present a wider angular range (>55˚) and a slightly better detection limit (1-2 wt%) than that produced by a pXRD such as the Olympus TERRA. As outlined earlier, both the

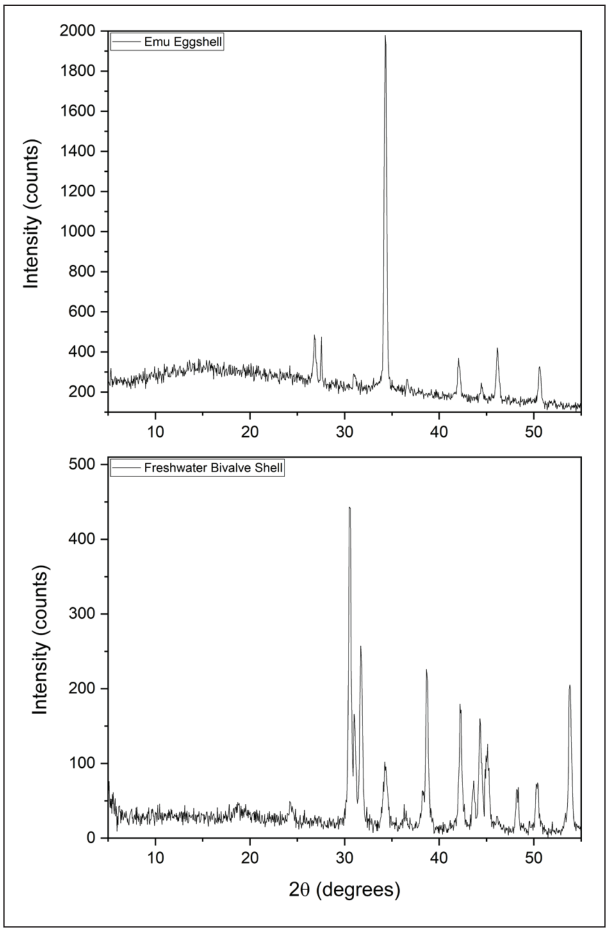

Figure 2. XRD diffractograms of emu (Dromaius novaehollandiae) eggshell (calcite) and freshwater bivalve (Alathyria jacksoni) shell (aragonite, calcite, quartz), using an Olympus TERRA pXRD analyser

benchtop and portable XRD systems present distinctive benefits and drawbacks, and ultimately the choice of using one of the two depends on several variables, including the research questions, available funds and time, level of expertise, and sampling constraints (e.g. sample preservation, sample location, regulations). As a rule of thumb, the portable XRD analyser would be efficient for a quick (on-site) screening of all the samples (with identification and quantification of all minerals), and for selecting the more complex mixtures that could be subsequently analysed via a benchtop XRD system.

XRD applications in Australian archaeological contexts

Broadly speaking, X-ray diffraction analysis identifies the mineralogical composition of materials, permitting an understanding of the conditions under which each material was formed and subsequently altered. XRD analysis presents a myriad of potential applications in Australian archaeological contexts, depending on specific research questions and type of samples, which may include faunal remains, lithic materials, ceramics, heat-retainers, ochres, and sediments.

Archaeofaunal remains such as fragments of bones, teeth, mollusc shell and eggshell are commonly found across the Australian landscape. The inorganic fraction of both bones and teeth is constituted by hydroxylapatite crystals. By studying the microstructural alterations of bone/tooth mineral crystallites, it may be possible to identify diagenetic and thermal processes that affected the faunal material (Piga et al. 2009; Rahmat et al. 2020; Rogers et al. 2010), which would help reconstructing ancient fire use and food processing (Solari et al. 2015; Van Hoesel et al. 2019), and/or post-mortem environmental conditions to which they were exposed (Stathopoulou et al. 2008; Trueman et al. 2004; Tütken et al. 2008).

Calcite, the inorganic fraction of avian eggshell, is also affected by heat-induced mineralogical changes, which are dependent on the temperature of heating (Engin et al. 2006; Macha et al. 2015; Naemchanthara et al. 2008; Tsuboi and Koga 2018). XRD analysis of mollusc shells and fish otoliths allows the identification of the different forms of calcium carbonate (aragonite and/or calcite) constituting their mineral fractions, which are indicative of the environmental conditions during the life of the animal and post-mortem. Environmental factors, such as chemical composition of water during shell formation, may affect the resulting shell mineralogy (Checa et al. 2007; Medaković et al. 2003). Moreover, mineralogical transition of aragonite into calcite may be later induced by heating as a result of food processing (Aldeias et al. 2019) or post-depositional thermal alteration (Milano and Nehrke 2018). The mineralogical characterization of the archaeofaunal remains is also a powerful tool for selecting well-preserved and reliable samples for DNA studies (Götherström et al. 2002), stable isotope analysis (Disspain et al. 2016; Munro et al. 2007), and radiocarbon dating (Long et al. 2018; Webb et al. 2007).

The determination of the mineralogical composition of lithic materials and earth-based pigments may help establish the provenance of raw materials by identifying the possible geological sources, and thus giving insight into procurement strategies and histories of transport and use (Corkill 2005; Dayet et al. 2016; Jercher et al. 1998; Trindade et al. 2010). Characterising the mineralogy of ochres may also solve attribution and authenticity issues of Indigenous artworks (Nel et al. 2010). The assessment of mineralogical changes in ceramics, heat-retainers, and other burnt clays allows for the reconstruction of their thermal history including the determination of firing events and maximum temperatures (Holakooei et al. 2014; Rasmussen et al. 2012). Clayey sediments and soils exposed to fire (hearths) undergo mineralogical alterations, which can be indicative of human occupation of the site and fire-related activities (Berna et al. 2007; Singh et al. 1991).

To conclude, the Olympus TERRA pXRD analyser may be a cost- and time-effective tool for characterizing, identifying, and sourcing (on-site and with minimal sample destruction) a range of archaeological materials that are routinely found in Australian contexts. Given its practicality, the use of a portable XRD could easily be implemented in routine archaeological investigations. If needed, more complex studies could subsequently be undertaken via a benchtop XRD system.

Acknowledgments

I would like to thank the anonymous reviewers for their helpful suggestions.

References

Aldeias, V., S. Gur-Arieh, R. Maria, P. Monteiro and P. Cura 2019 Shell we cook it? An experimental approach to the microarchaeological record of shellfish roasting. *Archaeological and Anthropological Sciences* 11(2):389–407

Berna, F, A. Behar, R. Shahack-Gross, J. Berg, E. Boaretto, A. Gilboa, I. Sharon, S. Shalev, S. Shilstein, N. Yahalom-Mack, J.R. Zorn, and S. Weiner 2007 Sediments exposed to high temperatures: Reconstructing pyrotechnological processes in Late Bronze and Iron Age Strata at Tel Dor (Israel). *Journal of Archaeological Science* 34(3):358–373

Checa, A.G., C. Jiménez-López, A. Rodríguez-Navarro and J.P. Machado 2007 Precipitation of aragonite by calcitic bivalves in Mg-enriched marine waters. *Marine Biology* 150(5):819–827

Corkill, T. 2005 Sourcing stone from the Sydney region: A hatchet job. *Australian Archaeology* 60(1):41–50

Dayet, L., F.-X. Le Bourdonnec, F. Daniel, G. Porraz and P.-J.Texier 2016 Ochre provenance and procurement strategies during the middle stone age at Diepkloof Rock Shelter, South Africa. *Archaeometry* 58(5):807–829

Disspain, M.C.F, S. Ulm, C. Izzo and B.M. Gillanders 2016 Do fish remains provide reliable palaeoenvironmental records? An examination of the effects of cooking on the morphology and chemistry of fish otoliths, vertebrae and scales. *Journal of Archaeological Science* 74:45–59

Downs, R.T. and MSL Science Team 2015 Determining mineralogy on Mars with the CheMin X-ray diffractometer. *Elements* 11(1):45–50

Engin, B., H. Demirtaş and M. Eken 2006 Temperature effects on egg shells investigated by XRD, IR and ESR techniques. *Radiation Physics and Chemistry* 75(2):268–277

Götherström, A., M.J. Collins, A. Angerbjörn and K. Lidén 2002 Bone preservation and DNA amplification. *Archaeometry* 44(3):395–404

Holakooei, P., U. Tessari, M. Verde and C. Vaccaro 2014 A new look at XRD patterns of archaeological ceramic bodies. *Journal of Thermal Analysis and Calorimetry* 118(1):165–176

Jercher, M., A. Pring, P.G. Jones and M.D. Raven 1998 Rietveld X-ray diffraction and X-ray fluorescence analysis of Australian Aboriginal ochres. *Archaeometry* 40(2):383–401

Long, K., R. Wood, I.S. Williams, J. Kalish, W. Shawcross, N. Stern and R. Grün 2018 Fish otolith microchemistry: Snapshots of lake conditions during early human occupation of Lake Mungo, Australia. *Quaternary International* 463:29–43

Macha, I.J., L.S. Ozyegin, F.N. Oktar and B. Ben-Nissan 2015 Conversion of ostrich eggshells (*Struthio camelus*) to calcium phosphates. *Journal of The Australian Ceramic Society* 51(1):125–133

Medaković, D., R. Slapnik, S. Popović and B. Gržeta 2003 Mineralogy of shells from two freshwater snails *Belgrandiella fontinalis* and *B. kuesteri*. *Comparative Biochemistry and Physiology Part A: Molecular & Integrative Physiology* 134(1):121–127

Milano, S. and G. Nehrke 2018 Microstructures in relation to temperature-induced aragonite-to-calcite transformation in the marine gastropod *Phorcus turbinatus*. *PloS one* 13(10):e0204577

Munro, L.E., F.J. Longstaffe and C.D. White 2007 Burning and boiling of modern deer bone: Effects on crystallinity and oxygen isotope composition of bioapatite phosphate. *Palaeogeography, Palaeoclimatology, Palaeoecology* 249(1–2):90–102

Naemchanthara, K., S. Meejoo, W. Onreabroy and P. Limsuwan 2008 Temperature effect on chicken egg shell investigated by XRD, TGA and FTIR. *Advanced Materials Research* 55–57:333–336

Nakai, I. and Y. Abe 2012 Portable X-ray powder diffractometer for the analysis of art and archaeological materials. *Applied Physics A* 106(2):279–293

Nel, P., P.A.. Lynch, J.S. Laird, H.M. Casey, L.J. Goodall, C.G. Ryan and R.J. Sloggett 2010 Elemental and mineralogical study of earth-based pigments using particle induced X-ray emission and X-ray diffraction. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* 619(1–3):306–310

Pecharsky, V. and P. Zavalij 2005 Fundamentals of diffraction. In V. Pecharsky and P. Zavalij (eds), *Fundamentals of powder diffraction and structural characterization of materials,* pp. 99–260. USA: Springer Science+Business Media

Piga, G., T.J.U. Thompson, A. Malgosa and S. Enzo 2009 The potential of X-ray diffraction in the analysis of burned remains from forensic contexts. *Journal of Forensic Sciences* 54(3):534–539

Rahmat, R.A., M.A. Humphries, J.J. Austin, A.M.T. Linacre, M. Raven and P. Self 2020 Integrating spectrophotometric and XRD analyses in the investigation of burned dental remains. *Forensic Science International* 310:110236

Rasmussen, K.L., G.A. De La Fuente, A.D. Bond, K.K. Mathiesen and S.D. Vera 2012 Pottery firing temperatures: A new method for determining the firing temperature of ceramics and burnt clay. *Journal of Archaeological Science* 39(6):1705–1716

Rogers, K., S. Beckett, S. Kuhn, A. Chamberlain and J. Clement 2010 Contrasting the crystallinity indicators of heated and diagenetically altered bone mineral. *Palaeogeography, Palaeoclimatology, Palaeoecology* 296(1–2):125–129

Singh, B., S. O'Connor, P. Veth and R. Gilkes 1991 Detection of amorphous alumino-silicate by X-ray diffraction and chemical analysis to detect firing in archaeological sediments. *Archaeology in Oceania* 26(1):17–20

Smith, D.K. 1998 Opal, cristobalite, and tridymite: Noncrystallinity versus crystallinity, nomenclature of the silica minerals and bibliography. *Powder Diffraction* 13(1):2–19

Solari, A., D. Olivera, I. Gordillo, P. Bosch, G. Fetter, V.H. Lara and O. Novelo 2015 Cooked bones? Method and practice for identifying bones treated at low temperature. *International Journal of Osteoarchaeology* 25(4):426–440

Stathopoulou, E.T., V. Psycharis, G.D. Chryssikos, V. Gionis and G. Theodorou 2008 Bone diagenesis: New data from infrared spectroscopy and X-ray diffraction. *Palaeogeography, Palaeoclimatology, Palaeoecology* 266(3–4):168–174

Trindade, M.J., M.I. Dias, J. Coroado and F. Rocha 2010 Firing tests on clay-rich raw materials from the Algarve basin (southern Portugal): Study of mineral transformations with temperature. *Clays and clay minerals* 58(2):188–204

Trueman, C.N., A.K. Behrensmeyer, N. Tuross and S. Weiner 2004 Mineralogical and compositional changes in bones exposed on soil surfaces in Amboseli National Park, Kenya: Diagenetic mechanisms and the role of sediment pore fluids. *Journal of Archaeological Science* 31(6):721–739

Tsuboi, Y. and N. Koga 2018 Thermal decomposition of biomineralized calcium carbonate: Correlation between the thermal behavior and structural characteristics of avian eggshell. *ACS Sustainable Chemistry & Engineering* 6(4):5283–5295

Tütken, T., T.W. Vennemann and H.-U. Pfretzschner 2008 Early diagenesis of bone and tooth apatite in fluvial and marine settings: Constraints from combined oxygen isotope, nitrogen and REE analysis. *Palaeogeography, Palaeoclimatology, Palaeoecology* 266(3–4):254–268

Van Hoesel, A., F.H. Reidsma, B.J.H. van Os, L. Megens and F. Braadbaart 2019 Combusted bone: Physical and chemical changes of bone during laboratory simulated heating under oxidising conditions and their relevance for the study of ancient fire use. *Journal of Archaeological Science: Reports* 28:102033

Webb, G.E., G.J. Price, L.D. Nothdurft, L. Deer and L. Rintoul 2007 Cryptic meteoric diagenesis in freshwater bivalves: Implications for radiocarbon dating. *Geology* 35(9):803–806