Shore-based X-ray fluorescence core scanning of IODP Expedition 369 (Australia Cretaceous Climate and Tectonics) material

Bogus, Kara; Batenburg, Sietske; Jones, Matthew; Edgar, Kirsty; De Vleeschouwer, David; Tagliaro, Gabriel; Martinez, Mathieu; Hanson, Emma; Walker-Trivett, Chloe; Levay, Brian; Schoemann, Mackenzie

Shore-based X-ray fluorescence core scanning of IODP Expedition 369 (Australia Cretaceous Climate and Tectonics) material

Kara Bogus*, Sietske Batenburg*, Matthew Jones*, Kirsty Edgar*, David De Vleeschouwer[1], Gabriel Tagliaro*, Mathieu Martinez*, Emma Hanson[2], Chloe Walker-Trivett[3], Brian Levay[4] and Mackenzie Schoemann[4]

*Expedition 369 shipboard scientist

[1]MARUM – Center for Marine Environmental Sciences, University of Bremen, Bremen, D-28359 Germany

[2]School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, B15 2TT United Kingdom

[3]Camborne School of Mines, University of Exeter, Penryn, TR10 9EZ United Kingdom

[4]IODP-JRSO, Texas A&M University, College Station, TX 77845 USA

1. Introduction and justification

Thick sections of recovered sediments and sedimentary rock from Expedition 369 sites (for an overview and site locations, please see the Expedition 369 summary chapter [Huber et al., 2019a]) were scanned on two X-ray fluorescence (XRF) core scanners (Avaatech B.V., Netherlands) hosted at the Gulf Coast Repository (College Station, TX, USA) from February through May 2018. These measurements were part of a new routine scanning program implemented by the International Ocean Discovery Program's JOIDES Resolution Science Operator (IODP-JRSO), and were undertaken primarily to aid in splice refinement and to guide sampling at the post-expedition sampling party (18–22 May 2018). Additionally, the XRF scanning datasets are valuable themselves and are planned for inclusion in post-expedition publications in the open literature (see the Expedition-related bibliography at http://publications.iodp.org/proceedings/369/369title.html).

Scientifically, measurement priorities were to scan intervals of high paleoclimatic importance (e.g., Oceanic Anoxic Events), spliced intervals from sites U1513, U1514 and U1516 to help refine the shipboard stratigraphy, and those with apparent cyclicity (sites U1512, U1513, U1514 and U1516) to aid astronomical tuning. Site U1515 was the only site not to have any sections scanned. Some of the intervals covered for paleoclimate included suspected OAEs 1d and 2 (Cenomanian–Turonian boundary), the Paleocene–Eocene Thermal Maximum (PETM), Eocene hyperthermals, Eocene–Oligocene boundary and Neogene sections. Full details of these intervals (visual expression, physical properties, geochemical characteristics and paleontological descriptions) can be found in the individual Proceedings volume site chapters (Huber et al., 2019b, 2019c, 2019d, 2019e).

2. Section preparation and scanning conditions

A targeted selection of archive-half split core sections from Exp. 369 sites was scanned (Table 1). For the majority of cores, the core catchers were not scanned because they either (1) were not long enough to fit into the scanner, (2) were poor quality or (3) were processed completely by the paleontology group on board; this is particularly the case for cores recovered with the Rotary Core Barrel (RCB, denoted by R in Table 1) system.

Before scanning, the instruments were first flushed with He to purge the system of air; He flow was maintained at about 30 mL/min during analyses. Additionally, at the beginning and end of each day, as well as several times during the day, a standard set of powders was analyzed to check for any immediate instrument issues (e.g., broken film, contamination). The spectra from the powders were also compared with older data to check for longer-term machine drift. These powders are only used to ensure machine performance, not to calibrate the core scan data, so all resulting data should be considered semi-quantitative.

Instrument performance was assumed to be good if (1) He was bubbling in the outflow bottle, (2) there were negative Ar values, (3) there was good separation of Kα and Kβ peaks for Ca and Fe and (4) the total counts per second (cps) were between 150,000 cps and about 300,000 cps.

To prepare the core sections, they were first allowed to equilibriate to room temperature overnight. Each section was then unwrapped and the split face was scraped with a clean glass slide. The surface of the core section was then examined visually for any measurement positions to skip or for areas of special interest to add. Cracks, fractures and voids were avoided. The split face of the section was then covered with thin (4 µm) polyethylene film (Ultralene) and loaded into the machine for analysis.

In total, just over 1050 m of core material was scanned. When possible, an entire site was scanned on the same machine. Exceptions to this can be found in Table 1. In general, sites U1512 and U1513 were scanned on the third generation Avaatech machine (XRF 1 in Table 1) and Site U1516 was scanned on the fourth generation Avaatech machine (XRF 2 in Table 1); Site U1514 was scanned on both. For sites that have stratigraphic splices (U1513, U1514 and U1516), entire sections were scanned, even if intervals within a section were not part of the shipboard splice.

All sections were scanned with 10 kV (0.160 mA, no filter) for major (e.g., Al, Si, Ca, Fe) and minor (e.g., K, Ti) elements, and most were also scanned at 30 kV (1.25 mA, thick Pd filter) primarily for Zr and/or 50 kV (0.75 mA, Cu filter) for Ba. The spot size was kept constant (cross-core slit = 12 mm, down-core slit = 10 mm). For 10 kV and 30 kV, the measurement time was 6 s per spot, while for 50 kV it was 10 s per spot. Additionally, all sections were scanned with thin (<1 mm) "feet" (spacers) placed on the metal ring at the bottom of the prism; these feet protect the film covering the prism from tearing and vastly decrease the number of film changes needed during scanning; however, it increases the distance between the split core surface and the detector and so can reduce the peak intensities, particularly for lighter elements (e.g., Al, Si, K and possibly Ca).

A variety of measurement resolutions (spanning 1 cm to 5 cm) were used depending on the sedimentation rates (calculated shipboard, see the individual Site chapters) and lithological features. Overall, a consistent resolution was attempted for each section, but ultimately varied depending on the continuity and condition of the split core surface (Table 1). It was generally easier to maintain a consistent resolution for the less lithified material recovered by the Advanced Piston Corer (APC; denoted H or F in Table 1) as the material was mostly continuous and did not present as many fractures/cracks. Fully lithified material, in many cases varied significantly from consistent measurement intervals, resulting in a less continuous resolution.

After analysis, the Ultralene was removed and the core sections were wrapped with plastic, placed back into D-tubes and moved back into the repository.

3. Data processing

The data were minimally processed after collection and both raw and processed data were uploaded to allow individual users to reprocess, manipulate and/or interpret the data at a later time. This is in line with the standard IODP-JRSO treatment of initial expedition data (e.g., shipboard data). Raw data were batch-processed using bAxil software (BrightSpec NV/SA, Belgium) and a data processing model specific for each energy condition. Briefly, bAxil allows a user to build a mathematical model that best describes the recorded experimental data (spectrum derived from each spot on a section). This is done by specifying the region of interest on a spectrum, choosing a background compensation method, identifying and selecting X-ray lines (elemental peaks) with their individual peak parameters (e.g., shape – Gaussian or Voight-profile), and establishing the correct values for energy calibration. The model parameters are then optimized by a non-linear least squares method (modified Levenberg-Marquardt algorithm) to minimize the sum of differences between experimental data and the model. These model templates were pre-loaded before scanning started and were general for the main lithology type encountered during Expedition 369; the models were not changed during the scanning period (i.e. February–May 2018). The data were quality controlled by (1) checking the throughput (total cps) at each spot (>200,000 cps; vast majority were >250,000 cps), (2) comparing the model fit results with the raw spectra. After these quality control steps were performed by either the scientist scanning the core sections that day or the XRF laboratory manager, the data were then uploaded into LIMS Reports. Section-level information can be found through the IODP-JRSO website (http://web.iodp.tamu.edu/LORE), and all of the data (raw and processed) are publicly available for download.

References

Huber, B.T., Hobbs, R.W., Bogus, K.A., Batenburg, S.J., Brumsack, H.-J., do Monte Guerra, R., Edgar, K.M., Edvardsen, T., Garcia Tejada, M.L., Harry, D.L., Hasegawa, T., Haynes, S.J., Jiang, T., Jones, M.M., Kuroda, J., Lee, E.Y., Li, Y.-X., MacLeod, K.G., Maritati, A., Martinez, M., O'Connor, L.K., Petrizzo, M.R., Quan, T.M., Richter, C., Riquier, L., Tagliaro, G.T., Wainman, C.C., Watkins, D.K., White, L.T., Wolfgring, E., Xu, Z., 2019a. Expedition 369 summary. *In* Hobbs, R.W., Huber, B.T., Bogus, K.A., and the Expedition 369 Scientists, *Australia Cretaceous Climate and Tectonics*. Proceedings of the International Ocean Discovery Program, 369: College Station, TX (International Ocean Discovery Program). https://doi.org/10.14379/iodp.proc.369.101.2019

Huber, B.T., Hobbs, R.W., Bogus, K.A., Batenburg, S.J., Brumsack, H.-J., do Monte Guerra, R., Edgar, K.M., Edvardsen, T., Garcia Tejada, M.L., Harry, D.L., Hasegawa, T., Haynes, S.J., Jiang, T., Jones, M.M., Kuroda, J., Lee, E.Y., Li, Y.-X., MacLeod, K.G., Maritati, A., Martinez, M., O'Connor, L.K., Petrizzo, M.R., Quan, T.M., Richter, C., Riquier, L., Tagliaro, G.T., Wainman, C.C., Watkins, D.K., White, L.T., Wolfgring, E., Xu, Z., 2019b. Site U1512. *In* Hobbs, R.W., Huber, B.T., Bogus, K.A., and the Expedition 369 Scientists, *Australia Cretaceous Climate and Tectonics*. Proceedings of the International Ocean Discovery Program, 369: College Station, TX (International Ocean Discovery Program). https://doi.org/10.14379/iodp.proc.369.103.2019

Huber, B.T., Hobbs, R.W., Bogus, K.A., Batenburg, S.J., Brumsack, H.-J., do Monte Guerra, R., Edgar, K.M., Edvardsen, T., Garcia Tejada, M.L., Harry, D.L., Hasegawa, T., Haynes, S.J., Jiang, T., Jones, M.M., Kuroda, J., Lee, E.Y., Li, Y.-X., MacLeod, K.G., Maritati, A., Martinez, M., O'Connor, L.K., Petrizzo, M.R., Quan, T.M., Richter, C., Riquier, L., Tagliaro, G.T., Wainman, C.C., Watkins, D.K., White, L.T., Wolfgring, E., Xu, Z., 2019c. Site U1513. *In* Hobbs, R.W., Huber, B.T., Bogus, K.A., and the Expedition 369 Scientists, *Australia*

Cretaceous Climate and Tectonics. Proceedings of the International Ocean Discovery Program, 369: College Station, TX (International Ocean Discovery Program). https://doi.org/10.14379/iodp.proc.369.104.2019

Huber, B.T., Hobbs, R.W., Bogus, K.A., Batenburg, S.J., Brumsack, H.-J., do Monte Guerra, R., Edgar, K.M., Edvardsen, T., Garcia Tejada, M.L., Harry, D.L., Hasegawa, T., Haynes, S.J., Jiang, T., Jones, M.M., Kuroda, J., Lee, E.Y., Li, Y.-X., MacLeod, K.G., Maritati, A., Martinez, M., O'Connor, L.K., Petrizzo, M.R., Quan, T.M., Richter, C., Riquier, L., Tagliaro, G.T., Wainman, C.C., Watkins, D.K., White, L.T., Wolfgring, E., Xu, Z., 2019d. Site U1514. *In* Hobbs, R.W., Huber, B.T., Bogus, K.A., and the Expedition 369 Scientists, *Australia Cretaceous Climate and Tectonics*. Proceedings of the International Ocean Discovery Program, 369: College Station, TX (International Ocean Discovery Program). https://doi.org/10.14379/iodp.proc.369.105.2019

Huber, B.T., Hobbs, R.W., Bogus, K.A., Batenburg, S.J., Brumsack, H.-J., do Monte Guerra, R., Edgar, K.M., Edvardsen, T., Garcia Tejada, M.L., Harry, D.L., Hasegawa, T., Haynes, S.J., Jiang, T., Jones, M.M., Kuroda, J., Lee, E.Y., Li, Y.-X., MacLeod, K.G., Maritati, A., Martinez, M., O'Connor, L.K., Petrizzo, M.R., Quan, T.M., Richter, C., Riquier, L., Tagliaro, G.T., Wainman, C.C., Watkins, D.K., White, L.T., Wolfgring, E., Xu, Z., 2019e. Site U1516. *In* Hobbs, R.W., Huber, B.T., Bogus, K.A., and the Expedition 369 Scientists, *Australia Cretaceous Climate and Tectonics*. Proceedings of the International Ocean Discovery Program, 369: College Station, TX (International Ocean Discovery Program). https://doi.org/10.14379/iodp.proc.369.107.2019