Certification Report of Apatite-NP-B01

Processing and certification of a microanalytical reference material including its way from apatite crystals to Nano-Pellets

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Abstract

The microanalytical certified reference material (CRM) Apatite-NP-B01 is designed for use by laboratories undertaking the determination of major and trace element mass fractions in apatite and equivalent matrices with LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry). U-Pb and Sr isotope ratios have been analysed using ID-TIMS, homogeneity and stability testing will be done as well in order to certify these parameters as well. The original apatite crystals were crushed. The resulting powder was subjected to a material-specific milling protocol, freeze-dried, homogenised, and split into batches, resulting in the material Apatite-NP. All batches are sufficient for approximately 10.000 units, which should make it available for the foreseeable future. Batch number 1 was pressed, into 10 mm diameter nanoparticulate pressed powder pellets, without any binders using a programmable hydraulic press.
This report describes the selection, production, and characterisation of the material.

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1. Introduction

Apatite ($Ca_5(PO_4)_3$ (OH,F,Cl)) is a ubiquitous accessory mineral which is has both scientific as well as industrial uses. Scientifically, it used for provenance investigation, petrogenesis and U-Pb age determination. Industrially it is sought after for its high phosphorous and rare earth element content. The advent of in situ microanalytical tools, such as laser ablation inductively coupled mass spectrometry (LA-ICP-MS), allows the direct analysis of samples without tedious sample preparation. A key to improved data quality in LA-ICP-MS is the use of matrix-matched reference materials. A general lack of such materials has been acknowledged in the literature[1]. Therefore, this material intends to cater to the needs of both the scientific as well as the industrial community.

2. Starting Material

A total amount of 5 kg of apatite crystals were purchased from Mikon GmbH, a mineral dealership. The crystals ranged from 10-50 mm in size (Fig. 1). Their source, according to the dealership is a mine in the Arusha Loliondo district in Tanzania, Africa.

Fig. 1 Photograph of the apatite crystals and a Nano-Pellet made from them.

To verify the identity of the material in accordance with ISO 17034:2017[2] the mineralogical characteristics, i.e., colour, hardness (Mohs), were identified and streak. Additionally, an X-ray diffraction (XRD) analysis was performed. The diffractogram confirms the identity (Fig. 2).

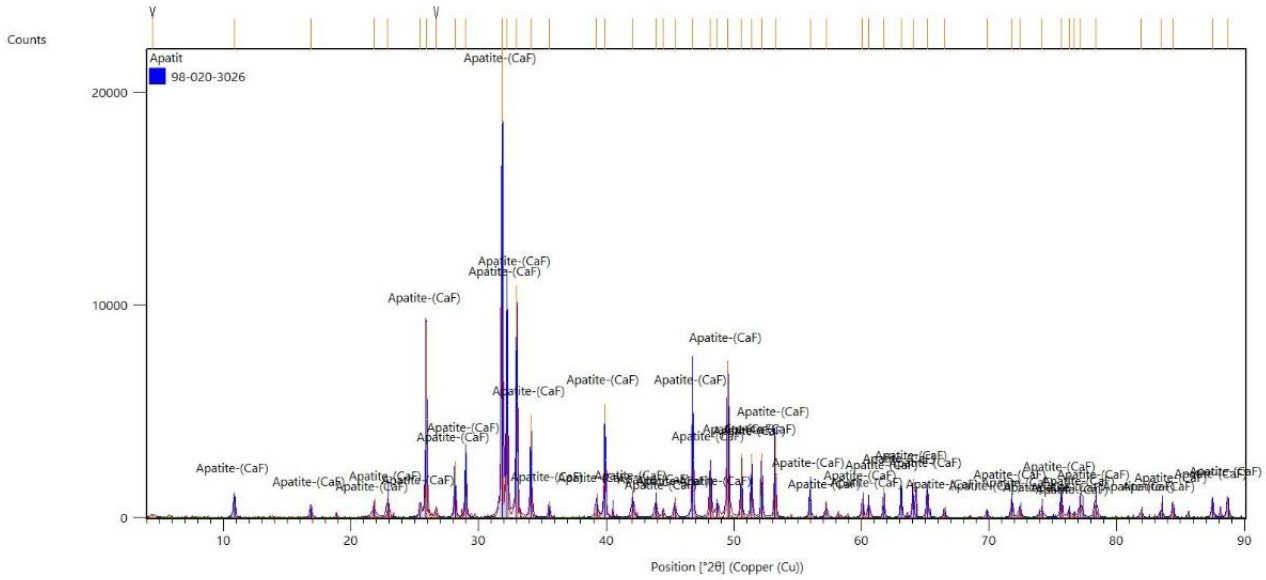

Fig. 2 X-ray diffractogram of powdered crystals confirming the identity as apatite.

3. Sample Preparation

The first preparation step was removing dirt and dust using distilled water. Thereafter, the crystals were placed in a bath of 1 % v/v nitric acid (HNO_3) to remove superficial contamination. Subsequently, they were rinsed using deionised water (18,2 MΩ resistivity) and dried in a laminar flow hood.

Approximately 1.5 kg of the cleaned crystals were crushed in a pre-cleaned jaw crusher to a particle size of ≤ 1 mm. This size fraction was further milled and sieved to a particle size of ≤ 63 µm in an agate vibratory disc mill and automatic sieving tower respectively.

The final grinding step was performed using our patented milling technique. The resulting slurry was freeze-dried, homogenised in a mixer-mill and split into batches of 12-15 g using a rotary sample splitter. The variability in the amount per batch is due to the degree of slight compression or lack thereof when filling the powder into hydrolytic class 1 glass vials for storage. A total of 86 batches were made.

Finally, batch number 1 (B01) was pressed into Nano-Pellets (10 mm diameter) resulting in a total of 117 units.

4. Homogeneity & Stability Testing

The homogeneity test was performed on the pellets (final packaged form). For this purpose, the samples were taken according to a random stratified sampling strategy. The number of units recommended to perform a homogeneity study are outlined in ISO Guide 35:2017[4]. For batches > 100 units equation 1 is suggested.

$$N_{min} = \max\left(10, \sqrt[3]{Units_{produced}}\right) \quad (1)$$

This means the minimum recommended number of units for batches of > 100 units is the larger of the two terms in parenthesis. This means 10 units were chosen for the homogeneity study as $10 > \sqrt[3]{117}$.

Homogeneity testing was performed adapting a procedure from the ASTM Guide E-826-14[3]. To transfer this procedure to LA-ICP-MS, the pellet surface was divided into seven analytical zones (Fig. 3). However, instead of making three repeated measurements on the same spot, three repeated measurements in close proximity were made (n=21). In total the homogeneity test is comprised of 210 spot measurements. The three results (a, b, c) in each analytical zone are then averaged, so each pellet contributes 7 results for the calculation of the uncertainty component pertaining to homogeneity. The resulting data were reduced using the software LADR (Norris Scientific Pty. Ltd.). The uncertainty component resulting from homogeneity was calculated following Annex C.1 in ISO Guide 35:2017.

Stability and its uncertainty component were assessed and calculated following Annex E.2 in ISO Guide 13528:2015[5]. Therefore, two randomly chosen pellets which had been placed in an oven at 60 °C for 8 h to simulate shipping in the back of a warm delivery vehicle. This assesses short-term stability. Long-term stability will be assessed in intervals of 4, 8 and 12 months. After successful assessment the stability will be monitored annually.

Ultimately, the usability of an uncertainty is determined by the manufacturer and the reference materials' intended use. Therefore, the Horwitz equation[6] and Horwitz Ratio (HORRAT) (eq. 2 & 3) was used to provide a mathematical basis for determining the usability of an uncertainty.

$$RSD_{Horwitz} = 2 \times Concentration^{(-0{,}1505)} \quad (2)$$

$$HORRAT = \frac{RSD_{Measured}}{RSD_{Horwitz}} \quad (3)$$

A HORRAT of ≤ 1 is ideal, between 1 and 2 acceptable and > 2 unacceptable.

A working example of such evaluations can be found here:

Example of our Data Evaluation for Certified Values

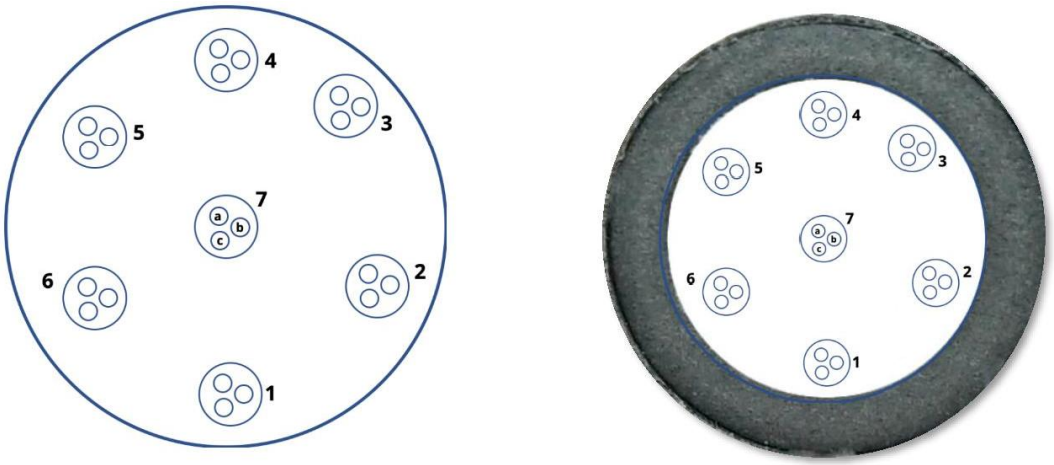

Fig. 3 Ablation pattern adapted from ASTM Guide E826-14.

5. Characterisation & Value Assignment

The characterisation approach applied was:

"Characterisation of a non-operationally defined measurand using two or more methods of demonstrable accuracy in one or more competent laboratories"

For characterisation of major and trace elements 16 aliquots of the Apatite-NP powder were analysed in two accredited (ISO 17025:2017) laboratories using a variety of digestions and analytical techniques. These include 4-acid digestion (hydrochloric acid HCl, nitric acid HNO_3, hydrofluoric acid HF and perchloric acid $HClO_4$) and lithium borate fusion followed by ICP-MS, ICP-OES and XRF analyses. For the characterisation of Uranium-Lead (U-Pb) ratios for age determination 18 aliquots of the Nano-Powders were analysed at the University of Geneve and GFZ Potsdam, using ID-TIMS (isotopic dilution thermal ionisation mass spectrometry), respectively. The Sr isotope ratios were determined by ID-TIMS analysis at IsoAnalysis UG measuring 3 aliquots.

Certified and information values can be found in the Certificate of Analysis here:

Certificate of Analysis

The assigned values and the uncertainty component resulting from the characterisation were calculated using equation 4 and 5.

$$Assigned\ Value = \frac{\sum accepted\ data\ set\ means}{number\ of\ data\ sets} \quad (4)$$

$$Uncertainty_{Characterisation} = \frac{Std.\,Dev.\,of\ data\ set\ means}{\sqrt{number\ of\ data\ sets}} \quad (5)$$

To use equations 4 & 5 the data set means must show an approximately normal distribution. This prerequisite was tested using the software XLSTAT.

Finally, each certified value needs to be accompanied by a combined expanded uncertainty at the 95 % CL. The uncertainty is calculated (eq. 6) by combining the uncertainty components from characterisation as well as homogeneity- and stability testing.

$$Unc._{Final} = k \times \sqrt{Unc._{Homog.}^2 + Unc._{Char.}^2 + Unc._{Stabil.}^2} \quad (6)$$

The expansion factor k is determined by the effective degrees of freedom and their corresponding value in Student's t-distribution. The coverage factor was applied to reach a confidence level of 95 %, as defined in the Guide to the Expression of Uncertainty in Measurement (GUM)[7]. According to ISO Guide 35:2017 it is permissible to use an expansion factor of 2 if there are ≥ 10 degrees of freedom. If there are < 10 degrees of freedom the appropriate factor should be taken from a Student's-t table, i.e., the distribution at the desired confidence level.

Here (eq. 7 & Tab. 1) is an example on how the final uncertainty is calculated:

Tab. 1 Calculation of the final combined and expanded uncertainty, using the analyte Uranium as an example.

	Certified Value	**Unit**
Uranium (U)	31.9	µg/g
$Uncertainty_{Chacaterisation}$	0.2	µg/g
$Uncertainty_{Homogeneity}$	0.9	µg/g
$Uncertainty_{Stability}$	0.6	µg/g
Expansion factor (k)	2	[-]

$$Unc._{Final} = 2 \times \sqrt{0.2^2 + 0.9^2 + 0.6^2} = 2.2 \quad (7)$$

Analyte [µg/g]	**Certified Value**	**Expanded Uncertainty @ 95 % CL**
Uranium (U)	31.9	2.2

6. Minimal Sample Size

Every CRM must have a statement of its minimal sample size. Minimal sample size for powdered certified reference materials is typically given in milligrams (mg). LA-ICP-MS analyses only take subsamples of e.g. a pressed powder pellet, meaning, that the mass of the powder used to make the pellet becomes irrelevant.

Therefore, the minimal sample size was determined by the spot -size used during the homogeneity- and stability test, which in the case of Apatite-NP-B01 was 50 µm. Further ablation conditions and signal acquisition parameters are shown in Tab. 2.

Tab. 2 Ablation and signal acquisition parameters during homogeneity- and stability-testing.

Laser fluence	6 J/cm^2
Repetition rate	10 Hz
Background	20 s
Signal acquisition	30 s

7. Acknowledgements

We would like to thank Dr. Axel Sjöqvist of Axray Scientific AB and Thomas Zack of the University of Gothenburg for their tireless efforts during the LA-ICP-MS analyses and providing high-quality data sets. Further gratitude goes to Prof. Urs Schaltegger and Dr. André Navin Paul from the University of Geneva as well as Dr. Patrick Carr (Université Lorraine) and Prof. Rolf Romer (GFZ Potsdam) for providing excellent U-Pb data. Finally, we would like to thank Dr. Martin Rosner from IsoAnalysis UG for providing exceptional Sr isotope ratio data.

8. References

[1] Chew DM, Sylvester PJ, Tubrett MN (2011), *U-Pb and Th-P dating of apatite by LA-ICPMS.* Chemical Geology 280: 200-216

[2] EN ISO 17034:2016 (D/E), *General requirements for the competence of reference material producers*

[3] ASTM E826-14, *Standard Practice for Testing Homogeneity of a Metal Lot or Batch in Solid Form by Spark Atomic Emission Spectroscopy.* ASTM International, West Conshohocken, PA, 2014. www.astm.org

[4] ISO Guide 35:2017 (E), *Reference materials – Guidance for characterization and assessment of homogeneity and stability*

[5] ISO 13528:2015 (E), *Statistical methods for use in proficiency testing by interlaboratory comparison*

[6] Horwitz, W., Albert, R. (1995), *Precision in analytical measurements: Expected values and consequences in geochemical analyses.* Fresenius Journal of Analytical Chemistry. 351:507-513

[7] ISO/IEC Guide 98-3:2008, *Uncertainty of measurement - Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

9. Document History

Version	*Date*	*Changes applied*
1.0	15.02.2022	First publication
1.1	21.07.2022	Links adapted to the new website