Guide to in-situ Rb-Sr Geochronology & The McArthur River Zn-Pb-Ag Deposit.

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Welcome to the first ever "Guide to Geo", thank you for subscribing! This article is focused on Rb-Sr geochronology and includes an interesting case study from the McArthur River Zn-Pb-Ag deposit. Our specialist co-author this week is Dr. Darwinaji Subarkah.

Introduction to Rb-Sr Geochronology

In 1906 the world was first introduced to the natural radioactivity of ^{87}Rb by Campbell & Wood (1). Thirty-two years later, Hahn & Walling (2) pioneered the Rb-Sr dating technique, which has continued to be refined to this day. The Rb-Sr dating technique utilizes the radioactive decay of ^{87}Rb to ^{87}Sr, which has a half-life of 49.61 ± 0.16 Ga (3). With reference to Figure 1, the rock/mineral of interest has a natural $^{87}Sr/^{86}Sr$ ratio called the initial value *(the straight blue line at the bottom of the Figure 1)*. Over time ^{87}Rb decays to ^{87}Sr, which forms an isochron *(the red dotted line in Figure 1)*. The slope of this isochron is time dependent. Older ages will have a steeper slope due to the production of more radiogenic ^{87}Sr, while younger ages will have a shallower slope due to having relatively less radiogenic ^{87}Sr. Thus, the slope of this line allows us to calculate the time since the mineral/rock was last at its initial $^{87}Sr/^{86}Sr$ ratio. To produce a spread across the isochron and ensure the highest precision possible, analyzing different minerals that contain various initial $^{87}Rb/^{86}Sr$ ratios (spread across the blue line) is preferred. As Rb has a similar size and charge to K, it will tend to be concentrated in K-rich minerals such as biotite, illite, and K-feldspar, therefore possessing relatively high $^{87}Rb/^{86}Sr$ ratios. As Sr is similar in size and charge to Ca, it will tend to be concentrated in Ca-rich minerals such as anorthite, clinopyroxene, calcite and apatite, and therefore possess relatively low $^{87}Rb/^{86}Sr$ ratios (see Figure 1). However, minerals such as biotite often contains a natural variation in $^{87}Rb/^{86}Sr$ ratios and therefore can be used solely to obtain a meaningful Rb-Sr age.

Old vs New Method

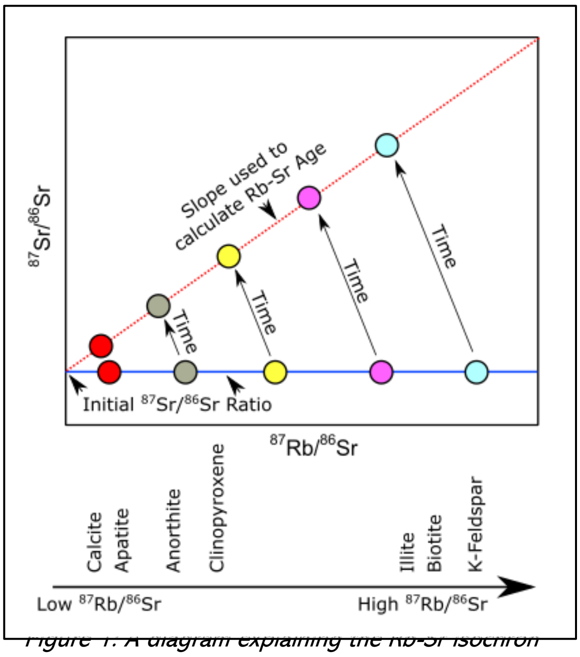

Figure 1: A diagram explaining the Rb-Sr isochron and the relative positioning of the $^{87}Rb/^{86}Sr$ ratio of various minerals.

One of the main obstacles that must be overcome with Rb-Sr geochronology is the isobaric interface between ^{87}Rb and ^{87}Sr (as these elements have the same mass, it's quite hard to get the mass spectrometer to tell them apart). The "old method", or more accurately the traditional method relied on whole-rock samples. This involved first crushing the rock to separate out the various mineral phases, using column ion chromatography to separate the various Rb and Sr phases, then doping the material with an enriched tracer before analyzing the material using Thermal Ionization Mass Spectrometry (4). In short, the old method is laboratory intensive, expensive and results often take months to produce. Moreover, as this method involved dissolving and analyzing whole-rock samples, it may also lead to mixed signatures and an overall geologically meaningless age. However, the advantage of this method is that the results are often very precise, containing errors proportional to <0.5-1% of the produced age (5). The new method uses a Laser Ablation system coupled to a Mass Spectrometer with an additional cell that contains N_2O gas used to separate ^{87}Sr from ^{87}Rb, and overcoming the isobaric interference problem (6). This approach is as easy as mounting an appropriate sample into a resin block, polishing it, and putting it into the laser. Hundreds of analyses can be performed a day using this method. This technique also preserves the textural composition of your sample, where particular minerals of interest (for example, biotite in a cross-cutting vein) can be targeted for analyses. So although this new method may produce ages that are relatively less precise (errors proportional to 2% to >5% of the obtained age), they are likely to be more accurate (7). In addition, the new method also allows the user to collect trace elements at the same time as Rb-Sr geochronology, which can be used to differentiate potential age populations.

Case Study – McArthur River

The McArthur River Zn-Pb-Ag deposit is located 700 km southeast of Darwin, Northern Territory, and is one of the largest known occurrences of Zn in Australia. Zn-Pb-Ag mineralization is constrained to the HYC Pyritic Shale Member of the ca. 1640 Ma Barney Creek Formation (8). The ore deposit consists of 8 individual ore lenses range from <2 to >12 m thick separated by barren sedimentary breccias as well as pyritic and dolomitic interbeds (8,9). Mineralization occurs as stratabound layers containing varying proportions of fine-grained pyrite, sphalerite and galena. As McArthur River is a Zn-Pb-Ag deposit, the age of mineralization cannot be determined by U-Pb geochronology, as it is almost certain that there will be large interference from non-radiogenic Pb. Furthermore, the fine-grained (<50 μm) size of the individual minerals that make up the shale do not allow for the newly developed Lu-Hf techniques to be used. Recently, an article by Subarkah (11) used in-situ Rb-Sr geochronology to differentiate between the age of unaltered shales and altered shales. Furthermore, ablating several clay-size minerals in one analysis has previously been done effectively using this same method to constrain the age of fault reactivation in deep crystalline basements (12). As the newly developed Rb-Sr method can be used on shales (which are made up of many individual fine-grained components), the McArthur River Zn-Pb-Ag deposit allows for the perfect test case to see if this method is capable of constraining the age of fine-grained Zn-Pb-Ag mineralization and/or associated alteration.

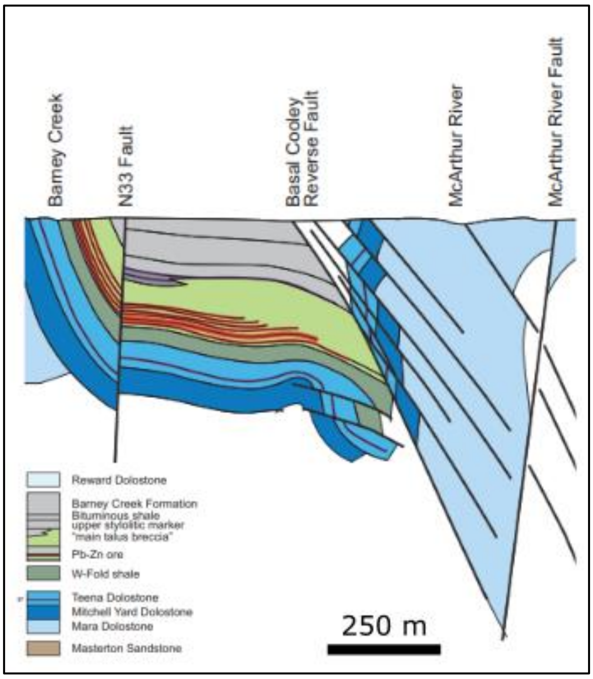

Figure 2: A cross section of the McArthur River Zn-Pb-Ag deposit edited from (10).

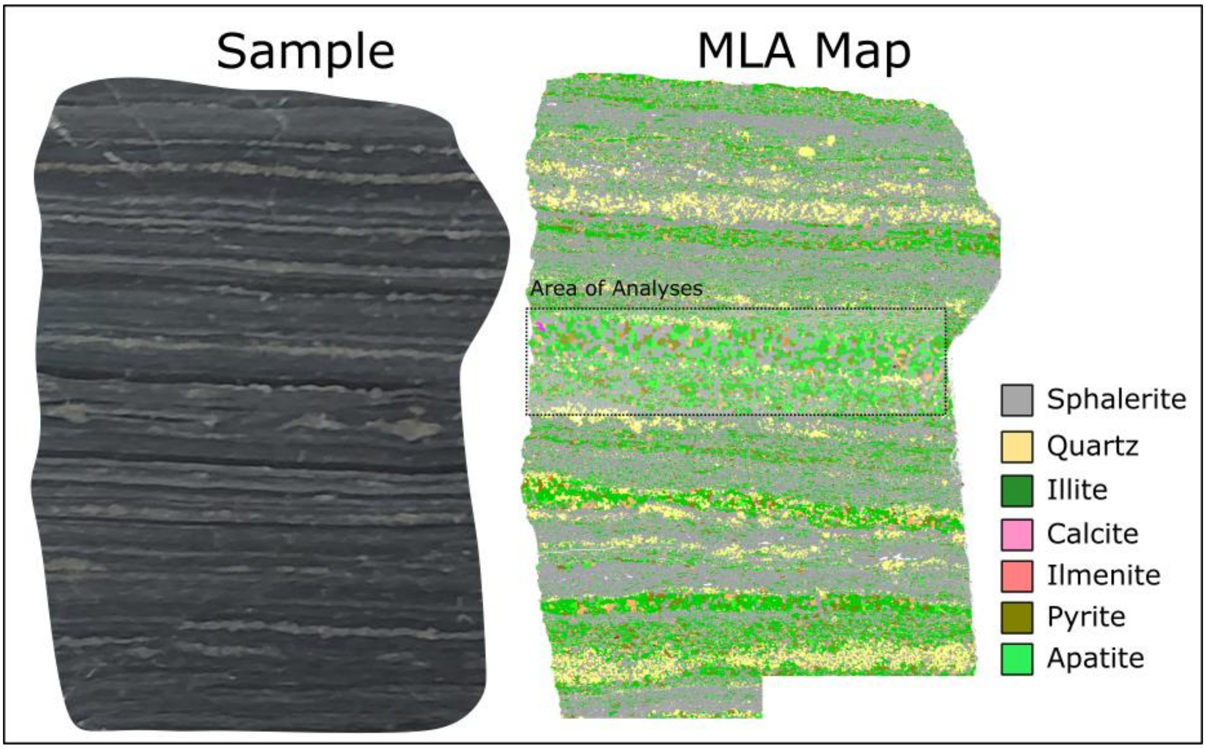

Figure 3: Image of the analysed sample and corresponding MLA maps.

The Sample

The sample selected for this study was collected from the historic selection at The University of Adelaide. Although this sample does not specify an exact location, it is labelled "*Ore Specimen – C21 Adit*". Mineral Liberation Analyses (MLA) maps were produced over this sample using the Scanning Electron Microscope (SEM) at Adelaide Microscopy. The sample is predominantly composed of sphalerite and fine-grained pyrite with variable amounts of quartz, illite, calcite, apatite, ilmenite and K-feldspar located throughout the host shale (Figure 3).

Method & Results

The analytical methods and data reduction techniques used for in study are outlined in (11). Sixty analyses were made across a selection of the sample least affected by Zn-Pb-Ag mineralization. All standard data as well as the data will be made available upon request. The 60 analyses produce a Rb-Sr isochron age of 1579 ± 57 Ma and an initial $^{87}Sr/^{86}Sr$ of 0.710 ± 0.013 (Figure 4).

Interpretation

The metallogenic model for the McArthur River has been the subject of recent debate. The traditional SEDEX model for McArthur River suggests that Zn-Pb-Ag mineralization was exhumed from a feeder fault and precipitated along the seafloor (8). Recently, based on geochemical modelling and textural evidence, it has been suggested that Zn-Pb-Ag mineralization formed along the sub-surface, during diagenesis or slightly after the consolidation of the host lithology (13,14). The 1579 ± 57 Ma age from Rb-Sr geochronology could be interpreted one of three different ways:

1 – This age could represent the age of Zn-Pb-Ag mineralization. If this is the case, it would be consistent with the age of mineralization during basin inversion and D_2 deformation of the Isan Orogeny (15). This also corresponds to the ceasing of sedimentation in the region. However, the age produced from this technique is within error of the depositional age of the shale, and therefore it cannot be used to differentiate

between an epigenetic or syn-diagenetic model for Zn-Pb-Ag mineralization.

2 – This age could represent a mixing signal between the age of alteration and the age of the shale. Although it would be difficult to assess if this is the case as the data forms a fairly linear line, it is possible that the age could be a mixing between the signal of the age of the 1639 ± 3 Ma (16) shale and the age of alteration. In this scenario, alteration associated with mineralization must be younger than the 1579 ± 57 Ma age produced from Rb-Sr geochronology.

3 – The age of Rb-Sr resetting in the area. A recent study by Subarkah (17) assessed the cooling age of Rb-Sr geochronology in shales, which is proposed to have a resetting temperature of approximately 120°C for systems involving fluid, or >190°C in dry systems. It is possible that this age could represent the time at which the shale cooled below 120°C or was reheated to a temperature above 120°C.

Conclusion:

The newly developed in-situ Rb-Sr geochronology method opens up a range of new possibilities in the geochronology world, especially in regions where U-Pb and Lu-Hf geochronology is unable to provide robust constrains (the fine-grained altered shale is the prime example). Although the method is comparably imprecise, offering errors of roughly 2% to >5% of the calculated age, it provides a new way to test hypothesis and constrain the age of hydrothermal, sedimentary, igneous and metamorphic processes. In this months GeoConverse, we tested this method on a sample from the McArthur River Zn-Pb-Ag deposit, producing an interesting age of 1579 ± 57 Ma, which can be interpreted to be the product of three different scenarios.

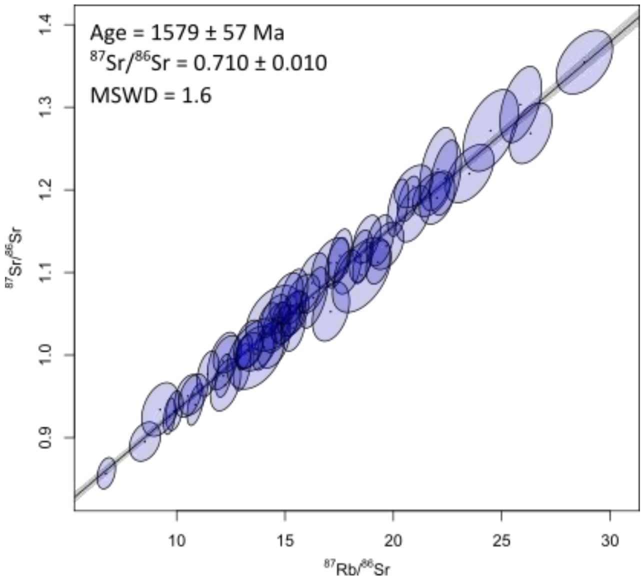

Figure 4: Results from Rb-Sr geochronology.

References:

1. Campbell N., Wood A. Radioactivity of the alkali metals. Proc Camb Philol Soc. 1906;14:15–21.

2. Hahn O, Walling E. Über die Möglichkeit geologischer Altersbestimmungen rubidiumhaltiger Mineralien und Gesteine. Zeitschrift für Anorg und Allg Chemie. 1938;236(1):78–82.

3. Villa IM, De Bièvre P, Holden NE, Renne PR. IUPAC-IUGS recommendation on the half life of 87Rb. Geochim Cosmochim Acta. 2015;164:382–5.

4. Nebel O. Rb–Sr Dating BT - Encyclopedia of Scientific Dating Methods. In: Jack Rink W, Thompson JW, editors. Dordrecht: Springer Netherlands; 2015. p. 686–98. Available from: https://doi.org/10.1007/978-94-007-6304-3_116

5. Nebel O, Scherer EE, Mezger K. Evaluation of the 87Rb decay constant by age comparison against the U–Pb system. Earth Planet Sci Lett. 2011;301(1–2):1–8.

6. Zack T, Hogmalm KJ. Laser ablation Rb/Sr dating by online chemical separation of Rb and Sr in an oxygen-filled reaction cell. Chem Geol. 2016;437:120–33.

7. Redaa A, Farkaš J, Gilbert S, Collins AS, Wade B, Löhr S, et al. Assessment of elemental fractionation and matrix effects during in situ Rb–Sr dating of phlogopite by LA-ICP-MS/MS: implications for the accuracy and precision of mineral ages. J Anal At Spectrom. 2021;36(2):322–44.

8. Large RR, Bull SW, Cooke DR, McGoldrick PJ. A genetic model for the HYC Deposit, Australia; based on regional sedimentology, geochemistry, and sulfide-sediment relationships. Econ Geol. 1998;93(8):1345–68.

9. Perkins WG, Bell TH. Stratiform replacement lead-zinc deposits; a comparison between Mount Isa, Hilton, and McArthur River. Econ Geol. 1998;93(8):1190–212.

10. Ahmad M, Dunster JN, Munson T. Ahmad M, Dunster JN and Munson TJ, 2013. Chapter 15: McArthur Basin: in Ahmad M and Munson TJ (compilers). 'Geology and mineral resources of the Northern Territory'. Northern Territory Geological Survey, Special Publication 5. In 2013. p. 15:1–15:72.

11. Subarkah D, Blades ML, Collins AS, Farkaš J, Gilbert S, Löhr SC, et al. Unraveling the histories of Proterozoic shales through in situ Rb-Sr dating and trace element laser ablation analysis. Geology. 2022;50(1):66–70.

12. Tillberg M, Drake H, Zack T, Kooijman E, Whitehouse MJ, Åström ME. In situ Rb-Sr dating of slickenfibres in deep crystalline basement faults. Sci Rep. 2020;10(1):1–13.

13. Spinks SC, Pearce MA, Liu W, Kunzmann M, Ryan CG, Moorhead GF, et al. Carbonate replacement as the principal ore formation process in the Proterozoic McArthur River (HYC) sediment-hosted Zn-Pb deposit, Australia. Econ Geol. 2021;116(3):693–718.

14. Liu W, Spinks SC, Glenn M, MacRae C, Pearce MA. How carbonate dissolution facilitates sediment-hosted Zn-Pb mineralization. Geology. 2021;

15. Gibson GM, Edwards S. Basin inversion and structural architecture as constraints on fluid flow and Pb–Zn mineralization in the Paleo–Mesoproterozoic sedimentary sequences of northern Australia. Solid Earth. 2020;11(4):1205–26.

16. Page RW, Sweet IP. Geochronology of basin phases in the western Mt Isa Inlier, and correlation with the McArthur Basin. Aust J Earth Sci. 1998;45(2):219–32.

17. Subarkah D, Nixon AL, Jimenez M, Collins AS, Blades ML, Farkaš J, et al. Constraining the geothermal parameters of in situ Rb–Sr dating on Proterozoic shales and their subsequent applications. Geochronology. 2022;4(2):577–600.