

Rb-Sr SYSTEMATICS OF UNGROUPED ACHONDRITES. Y. Amelin, Research School of Earth Sciences, The Australian National University, Canberra ACT 2601, Australia (yuri.amelin@anu.edu.au).

Introduction: Achondrites are rocks from asteroids that underwent melting and in some cases differentiation. Several achondrites found in the recent years have unique chemical and isotopic characteristics, and do not fit in the established groups. Studies of these meteorites give a glimpse of the diversity of asteroids that formed and partially melted in different domains in the accreting protosolar nebula, at different time, from different source materials, and under different conditions.

Most achondrites are depleted in moderately volatile elements including alkaline metals, and have low Rb/Sr ratio, and hence contain only small fraction of radiogenic ^{87}Sr produced *in situ*. It is therefore possible to calculate their initial $^{87}\text{Sr}/^{86}\text{Sr}$ with small uncertainty, and apply the initial Sr chronometer [1, 2] to determine the time of separation of their source material from the protosolar nebula.

Here I present ^{87}Rb - ^{87}Sr data for five ungrouped achondrites: NWA 8486, a mafic cumulate rock paired with NWA 7325 [3], Asuka 881394, the oldest known achondrite [4] that resembles cumulate eucrites in mineralogy but has non-HED oxygen isotope composition, and three unusual primitive achondrites NWA 6693, NWA 6704, and NWA 10132 [5-7]. All these meteorites have well-behaved U-Pb systems, and, with Pb-isotopic, $^{238}\text{U}/^{235}\text{U}$ -corrected ages between 4562-4566 Ma, are among the oldest and best preserved achondrites, and thus good candidates for initial Sr dating.

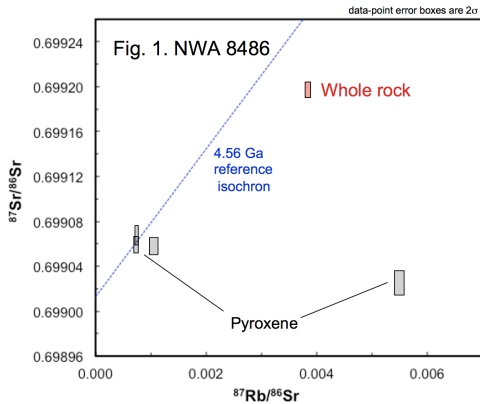
Methods: Analyses of pyroxene from NWA 8486, NWA 6693 and Asuka 881394 were conducted on mineral fractions prepared for U-Pb dating. This part of work had a dual purpose: to determine the initial $^{87}\text{Sr}/^{86}\text{Sr}$, and to evaluate the feasibility of a Rb-Sr study of achondrite minerals as a piggyback to the U-Pb dating (hence using cleaning procedures optimized for U-Pb dating), thereby optimizing the utilisation of rare and unique materials, saving the work involved in picking, cleaning and dissolution, and avoiding possible complications related to the sample heterogeneity in combined interpretation of U-Pb and Rb-Sr data. The pyroxene was hand-picked and cleaned using our standard procedures (e.g. [3, 8]) that include leaching in 0.5M HNO_3 , 7M HNO_3 , 6M HCl and 0.5M HF . Washes containing matrix elements including Rb and Sr were collected after Pb and U separation, and split into two aliquots: 10-40% aliquots for Rb and Sr concentration determinations with ^{85}Rb - ^{84}Sr spike, and 60-90% for isotope analysis of unspiked Sr.

An additional set of mineral fractions (olivine, pyroxene, plagioclase, and whole rock) was prepared for each of NWA 6693, NWA 6704, and NWA 10132. These fractions were thoroughly cleaned by repeated ultrasonic agitation in high purity water, but were not subjected to any acid leaching. The sample solutions were aliquotted for isotope dilution and isotopic composition measurements as above.

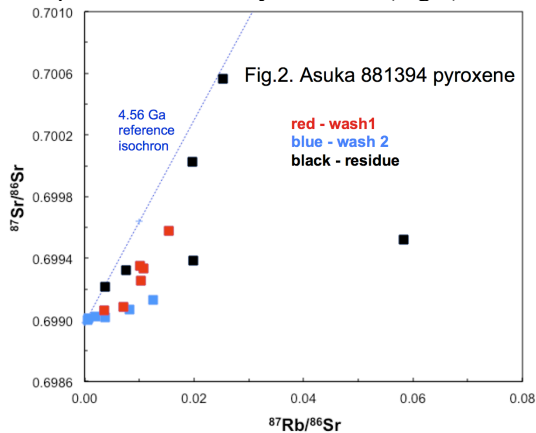
Strontium was separated on the columns packed with 50 μm of Eichrom Sr-spec resin, loaded on out-gassed Re filaments with TaF_5 solution [9], and analysed at the ANU on the TritonPlus TIMS in static mode with normalisation to $^{88}\text{Sr}/^{86}\text{Sr}=8.37521$, using amplifier rotation for the unspiked isotope composition runs. Analyses of the NIST SRM 987 standard during the course of this study yielded $^{87}\text{Sr}/^{86}\text{Sr} = 0.7102494 \pm 0.0000028$ (0.0004% 2SE, n=34) and $^{84}\text{Sr}/^{86}\text{Sr} = 0.0564905 \pm 0.0000010$ (0.0018% 2SE, n=34). All data are reported relative to $^{87}\text{Sr}/^{86}\text{Sr} = 0.71025$ in SRM 987. Rubidium was analysed without chemical separation by loading small aliquots (ca. 0.1-1% of the total spiked aliquot) on Re filaments with silicagel [10], and measuring on a modified MAT 261 TIMS. Average fractionation factor was determined by repeated analyses of natural Rb from dissolved mica, also without chemical separation.

The data are corrected for total procedure blanks of 2-4 pg Sr and 0.2-0.3 pg Rb measured in each session. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ are calculated using the Pb-isotopic ages of the respective achondrites, and the ^{87}Rb decay constant of $(1.3972 \pm 0.0045) \times 10^{-11} \text{ a}^{-1}$ recommended by the joint IUPAC-IUGS task group on isotope data in geosciences [11].

Results: Only residues from after acid washing were analysed for NWA 8486. Four pyroxene fractions and one whole rock contain 16-20 ppm Sr. Rb concentrations are between 4.5-33 ppb. Measured $^{87}\text{Sr}/^{86}\text{Sr}$ are between 0.69903 and 0.69920. The two fractions with the lowest $^{87}\text{Rb}/^{86}\text{Sr} < 0.001$ yield consistent initial $^{87}\text{Sr}/^{86}\text{Sr}$ with the weighted average value of 0.699019 ± 0.000013 (Fig.1). This value can be tentatively considered initial $^{87}\text{Sr}/^{86}\text{Sr}$ of NWA 8486. One pyroxene fraction has measured $^{87}\text{Sr}/^{86}\text{Sr} = 0.69903$, identical within uncertainty to the estimated initial, but it has also relatively high $^{87}\text{Rb}/^{86}\text{Sr} = 0.0055$, which yields an unreasonably low apparent initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.69867. This fraction clearly contained recently added Rb, either from terrestrial weathering or from processing.



Pyroxenes from Asuka 881394 have variable Sr concentrations between 1.8-30 ppm (calculated from analyses of washes and residues). The data show pervasive presence of recently added Rb (Fig.2).

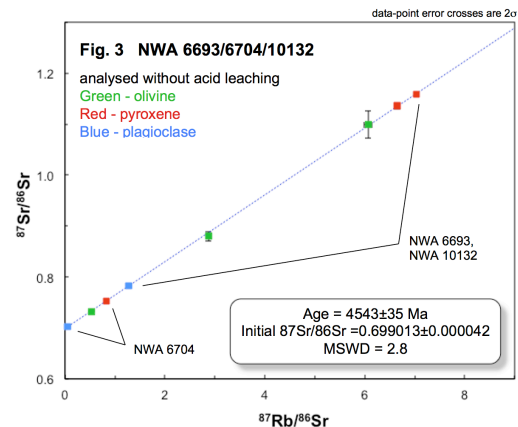


The measured and decay corrected data for the second washes of two Sr-rich fractions with low $^{87}\text{Rb}/^{86}\text{Sr}$ below 0.0007, yield the best estimate initial of 0.699984 ± 0.000018 . It is indistinguishable from the value of 0.699989 ± 0.000014 , determined by [12] from analysis of multiple minerals from that meteorite.

Compared to differentiated achondrites, the primitive (i.e. having approximately chondritic composition) achondrites NWA 6693/6704/10132 are Rb-rich and Sr-poor. Whole rock fraction of NWA 6693 contains 6.2 ppm Sr and 3.2 ppm Rb, close to the abundance of these elements in CI chondrites. The $^{87}\text{Rb}/^{86}\text{Sr}=1.5$ is higher than observed in most chondrites, and is extremely uncommon for achondrites. Pyroxene and olivine have lower Rb and Sr contents of 0.15-1.0 ppm, but even higher $^{87}\text{Rb}/^{86}\text{Sr}$ of 6.1-7.0. Plagioclase has higher Rb and Sr concentrations of 14 and 33 ppm, and lower (but still high) $^{87}\text{Rb}/^{86}\text{Sr}$ of 1.28. Rb and Sr concentrations in minerals from NWA 10132 are similar to those of NWA 6693. NWA 6704 shows less extreme Rb enrichment and Sr depletion, but the distribution of these elements between the minerals are similar. Whole rock and plagioclase of NWA 6704 have

$^{87}\text{Rb}/^{86}\text{Sr}$ of 0.054-0.101, sufficiently low to attempt calculation of the $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio.

Acid leachates and residues of NWA 6693 pyroxene show widely dispersed data, and very radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ up to 0.99. The data for unleached minerals and whole rocks from all three meteorites display much smaller dispersion than the leaching steps of the pyroxenes. Mineral fractions alone yield the best regression with only a small excess scattering (MSWD=2.8), corresponding to the age of 4543 ± 35 Ma and initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.699013 ± 0.000042 . The NWA 6693 data points re-combined from leachate and residue analyses plot on this isochron.



Discussion: With current precision of Sr isotope analysis, initial $^{87}\text{Sr}/^{86}\text{Sr}$ of achondrites can potentially yield precision of initial Sr dates relative to the solar nebula of 1 Ma or even better. Application of the initial Sr chronometer is hampered by the presence of Rb introduced in the terrestrial environments, and by decoupling of Rb and radiogenic Sr induced by the mineral cleaning procedures. The leaching induced disturbance can be undone by data re-combination, but verification by analysis of unleached fractions is desirable. The CAI reference initial $^{87}\text{Sr}/^{86}\text{Sr}$ [13, 14] needs improvement by additional analysis of best preserved CAIs with negligible Rb from several CV chondrites.

References: [1] Papanastassiou D.A., Wasserburg G.J. (1969) *EPSL* 5, 361-376 [2] Halliday A.N., Porcelli D. (2001) *EPSL* 192, 545-559 [3] Koefoed P. et al. (2016) *GCA* 183, 31-45, [4] Wadhwa M. et al. (2009) *GCA* 73, 5189-5201. [5] Warren P.H. et al. (2013) *GCA* 107, 135-154 [6] Irving A.J. et al. (2011) *74th MetSoc Meeting*, #5231 [7] Irving A.J. et al. (2015) *78th MetSoc Meeting*, #5254 [8] Iizuka T. et al. (2014) *GCA* 132, 259-273 [9] Charlier B.L.A., et al. (2006) *Chem. Geol.* 232, 114-133 [10] Huyskens M.H. et al. (2012) *JAAS* 27, 1439-1446 [11] Villa I.M. et al. (2015) *GCA* 164, 382-385 [12] Nyquist L.E. et al. (2011) *Formation of the First Solids in the Solar System*, #9037. [13] Hans U. et al. (2013) *EPSL* 374, 204-214. [14] Amelin Y. et al. (2015) *78th MetSoc Meeting*, #5388.