RUTILES AND ZIRCONS OF MESOSIDERITES: COMBINED NIOBIUM-ZIRCONIUM AND URANIUM-LEAD CHRONOMETRY AND THE INITIAL ABUNDANCE OF NIOBIUM-92 IN THE SOLAR SYSTEM.

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Introduction: The short-lived isotope ^{92}Nb decays to ^{92}Zr with a half-life of 37 Myr. The ^{92}Nb-^{92}Zr decay system has been recognized as a promising tool to provide chronological information on the evolution of planetary materials over a relatively long period in the early solar system [e.g., 1, 2]. The application of this chronometer to iron meteorites and mesosiderites that contain Nb-enriched rutile is particularly useful, because dating of these meteorites by other means is notoriously difficult. The initial ^{92}Nb/^{93}Nb ratio of the solar system is important for both ^{92}Nb-^{92}Zr chronometry and astrophysical studies on *p*-process nuclides [e.g., 3]. Previous estimates of this ratio range over several orders of magnitude from 10^{-5} to 10^{-3} [1, 4, 5, 6]. In particular, estimates from iron meteorites and mesosiderites vary between 10^{-5} and 10^{-3} and thus require further refinement [1, 4, 5, 6]. A recent study utilizing internal isochrons of angrites and eucrites revealed an initial ^{92}Nb/^{93}Nb ratio of $(1.7 \pm 0.6) \times 10^{-5}$ [2] in agreement with [1] and a homogeneous distribution in the formation regions of their parent bodies. Although the new study [2] significantly improved the estimate of the initial ^{92}Nb/^{93}Nb ratio (relative uncertainty: 35%), it did not address mesosiderites and iron meteorites. Moreover, a more precise determination of this ratio is still necessary for the useful application of the Nb-Zr chronometer to early solar system materials.

This study aims to determine, with high precision, the initial ^{92}Nb/^{93}Nb ratio of mesosiderites using accessory rutile and zircon thereby also addressing the geological history of their parent body. The reasons for using rutile and zircon are: (I) they have strong resistance to mechanical and chemical breakdown over long periods, (II) zircon and rutile are the primary host minerals of Zr and Nb, respectively and if they are cogenetic, this allows for precise isochrons with large variations in Nb/Zr ratios, and (III) the absolute crystallization age of rutile and zircon, which is needed to calculate the initial ^{92}Nb/^{93}Nb ratio of the solar system, can be determined by U-Pb dating of zircons.

Samples and Methods: Occurrence and chemical composition of rutiles in Vaca Muerta, Northwest Africa (NWA) 1242, Asuka (A) 882023, and Estherville mesosiderites were examined using SEM and EPMA at National Institute of Polar Research, Japan (NIPR). Rutile grains were separated from 10 g of Vaca Muerta, NWA 1242, and Estherville and 2 g of A 882023 by dissolving the metal parts in concentrated HCl and the silicate parts in concentrated HNO_3-HF mixture. Subsequently, rutile grains with sizes of ca. 20–50 μm in diameter were handpicked from the residues (200–700 grains for each sample). The grains were then dissolved in HNO_3-HF using Parr® bombs. The analytical procedure for the determination of ^{93}Nb/^{90}Zr ratios and Zr isotope compositions followed [2, 7]. The Zr isotope measurements were performed using a Neptune Plus MC-ICPMS coupled with an Aridus II introduction system at ETH Zurich. Zircons were handpicked from the residues of Estherville. The crystallinity of four zircons (70–200 μm in diameter) was checked using Raman microscopy at NIPR. Individual grains were cleaned with 3M HNO_3 before loading single crystals into 200 μl microcapsules. Samples were spiked with 3–5 mg of EARTHTIME ^{202}Pb-^{205}Pb-^{233}U-^{235}U tracer solution and dissolved in concentrated HF using Parr® bombs. Uranium and Pb were separated using a HCl-based column chemistry before being loaded on outgassed Re-filaments with a microdrop of Si-Gel ion emitter. Uranium and Pb isotope measurements were performed using a TRITON Plus TIMS at ETH Zurich [8]. The Zr+Hf+REE fractions of the U-Pb column chemistry were further processed for Zr isotope analyses. The Zr isotope composition of zircons was measured using MC-ICPMS following the same techniques as outlined above.

Results and Discussion:

Timing of rutile and zircon formation in mesosiderites. The rutiles from each sample yielded ^{93}Nb/^{90}Zr ratios of 12.7 ± 0.8 in Vaca Muerta, 9.9 ± 0.4 in NWA 1242, 1.61 ± 0.12 in A 882023, and 1.26 ± 0.08 in Estherville. The ^{93}Nb/^{90}Zr ratios decrease with increasing metamorphic grades of our samples from Vaca Muerta (1A) to NWA 1242 (2A), A 882023 (2/3A), and Estherville (3/4A). Since the metamorphic grades of mesosiderites were likely established during the metal-silicate mixing event [9] that mesosiderites experienced, the rutiles likely also formed during this event. Therefore, the Zr concentration of rutiles can be utilized as a thermometer as previously done for terrestrial rocks [e.g., 10]. Using the calibration of the Zr-in-rutile thermometer of [10], the crystallization temperatures of rutiles are estimated to 634°C for Vaca Muerta, 708°C for

NWA 1242, 755°C for A 882023, and 792°C for Estherville with an uncertainty of ± 50°C.

Mesosiderites have two kinds of zircons [11]: (I) relict zircons that crystallized before the mixing event, and (II) secondary zircons that formed through the mixing event. Typical secondary zircons show quite low U (~0.3 ppm) and Th (~0.04 ppm) contents because they formed after the incorporation of U, Th, and REE into abundant phosphate minerals [12]. Four zircon grains with U contents similar to those of the secondary zircons reported in [11] yielded a weighted mean ^{207}Pb-^{206}Pb age of 4528.4 ± 1.4 Ma (2σ). This age is in good agreement but significantly more precise than the previously reported age for the mixing event of 4519 ± 27 Ma [11]. The cooling rate of the mesosiderite parent body (MPB) after the mixing event was estimated to >1°C/100 years at high temperature (500–1150°C) [13], suggesting that the time lag between rutile and secondary zircon formation as well as differences in closure temperature for Nb-Zr in rutile and U-Pb in zircon can be neglected. Therefore, the rutiles and zircons used in this study can be considered as cogenetic minerals that formed during the mixing event at 4528 Ma.

Nb-Zr systematics of rutile and zircon in mesosiderites. The $\varepsilon^{92}Zr$ values of *rutiles* are 2.87 ± 0.21 for Vaca Muerta, 2.36 ± 0.13 for NWA 1242, 0.56 ± 0.19 for A882023, 0.26 ± 0.21 for Estherville, and that of a *zircon* from Estherville is 0.08 ± 0.02 (Fig. 1). The Vaca Muerta rutiles show the highest $\varepsilon^{92}Zr$ value obtained so far among published MC-ICPMS data [e.g., 1, 2, 6]. Furthermore, the zircon indicates a positive $\varepsilon^{92}Zr$ value, which, however, needs further confirmation. If correct, this positive value may be inherited from a previous generation of ilmenites. This is because secondary zircons in mesosiderites likely formed by reactions between silica and Zr released from ilmenite during high temperature metamorphism [11]. Early formed ilmenites display positive $\varepsilon^{92}Zr$ values due to high Nb/Zr ratios [1, 2].

The combined Nb-Zr data of rutiles and zircons define an initial $^{92}Nb/^{93}Nb$ ratio of $(7.6 \pm 0.4) \times 10^{-6}$ at the time of their formation in mesosiderites. Using the absolute age of zircons (4528.4 ± 1.4 Ma) yields an initial $^{92}Nb/^{93}Nb$ ratio of the solar system of $(1.57 \pm 0.09) \times 10^{-5}$ (relative uncertainty: 6%). This is consistent but significantly more precise than the estimates of [1, 2]. This new initial ratio is vital for absolute ^{92}Nb-^{92}Zr ages and astrophysical studies regarding *p*-process nucleosynthesis.

Usability of Nb-Zr chronometry based on meteoritic rutiles. The Nb-Zr data from rutiles alone define an initial $^{92}Nb/^{93}Nb$ ratio of $(7.5 \pm 0.7) \times 10^{-6}$. Using the solar system initial $^{92}Nb/^{93}Nb$ ratio from [2], this yields a ^{92}Nb-^{92}Zr age of rutiles of 45 ± 16 Myr after CAI (4567 Ma [14]). This age corresponds to the absolute age of 4522 ± 16 Ma, which is in good agreement with the ^{207}Pb-^{206}Pb age of zircons. Based on the ^{147}Sm-^{143}Nd ages of clasts from Vaca Muerta [15], which show younger ages (4.42–4.48 Ga), the MPB likely experienced local impacts after the global mixing event, which then reset some chronometers. The consistent age of rutiles and zircons in mesosiderites indicates that the Nb-Zr decay system in rutiles is very robust such that it was not modified by the later local impact events. This suggests that Nb-Zr systematics of meteoritic rutiles provides important chronological information for their parent bodies and is relatively immune to the effect of impact processing.

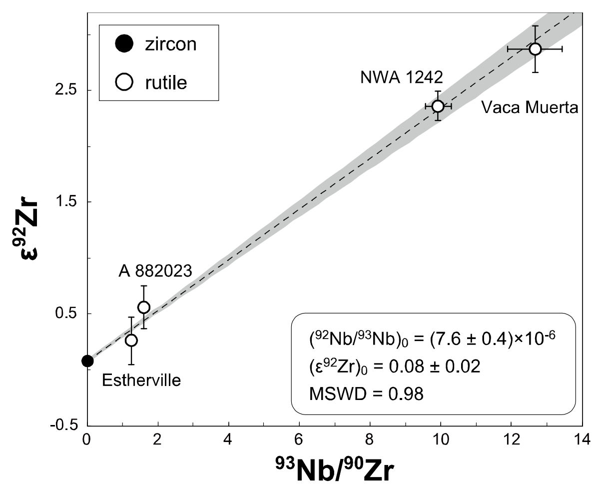

Fig. 1. Nb-Zr isochron diagram for mesosideritic rutiles and zircons. The isochron regression and error envelope (95% probability) are shown as a dotted line and gray area, respectively. The data-point errors are 2 σ.

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