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Meteoritic zircon – Occurrence and chemical characteristics

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ABSTRACT

In common with the remarkable variation in the bulk rock Zr content of distinct meteorite groups, ranging from <1 ppm to >800 ppm, the occurrence and abundance of accessory zircon is also highly diverse and limited to certain meteorite classes. A detailed literature study on the occurrence of meteoritic zircon, along with other Zr-bearing phases reveals that lunar rocks, eucrites and mesosiderites are the prime sources of meteoritic zircon. Rare zircon grains occur in chondrites, silicate-bearing iron meteorites and Martian meteorites, with grain sizes of >5 μm allowing chemical and chronological studies at high spatial resolution using secondary ion mass spectrometry (SIMS) technique. Grain sizes, crystal habits, structural and chemical characteristics of zircon grains derived from various meteorite types, including their REE abundances, minor element concentrations, and Zr/Hf values is diverse. Superchondritic Zr/Hf values (47 ± 8; s.d. with $n = 97$), i.e., typical for zircon in eucrites and mesosiderites, indicate crystallization from a fractionated, incompatible-element-rich (residual) melt. Differences in REE abundances, occurrence or absence of Ce- and Eu-anomalies, and overall REE patterns that are often fractionated with a depletion in LREE, might be primarily controlled by variable formation conditions of individual grains and/or differences in the residual melt compositions on a small, local scale within single samples. Subsequent fractionation/modification of the chemical fingerprint of meteoritic zircon can involve high-temperature annealing processes during thermal metamorphic reactions and/or impact events along with mixing of lithic fragments since many samples are breccias.

1. Introduction

The presently identified approximately 280 mineral species in meteorites reflect a wide variation in redox sensitive environments under which distinct meteorite groups and their components were formed, and in some cases unusual solar nebula formation conditions. Therefore, the occurrence of specific minerals that form under different redox-sensitive conditions, their chemical composition and the textural relationship are relevant for understanding the genesis of meteorites. The importance of zircon as an accessory, chemically inert and refractory mineral, is based on (i) its tendency to incorporate trace elements, including long-lived (^{238,235}U, ^{232}Th, ^{176}Lu), and short-lived (^{182}Hf) radionuclides, (ii) its chemical and physical durability, and thus high resistance to chronological resetting in a variety of geological processes over long periods of time and a range of P–T conditions, and (iii) its remarkable robustness to high temperature diffusive re-equilibration, weathering and transport processes, under dry conditions (e.g., Cherniak et al., 1997; Watson et al., 1997). For instance, the resistance of zircon to impact modification makes this accessory phase a valuable target for geochronologic studies, e.g., of impact-altered lunar rocks (Jolliff et al., 2003) and impact sites on Earth (e.g., Chicxulub impact site; Krogh et al., 1993). In addition to its dominant role in controlling Zr and Hf distribution, zircon can have significant influence on the behavior of heavy rare earth elements (HREE)$^{3+}$, Y^{3+}, Th^{4+}, U^{4+}, Nb^{5+} and Ta^{5+}, and some platinum-group-element (PGE). Their large ionic radii and high charge make these elements incompatible in many rock-forming silicate minerals and they generally become concentrated in the residual melts and are incorporated in the late-stage crystallizing zircon as the crystal structure of zircon accommodates widely varying proportions of trace elements (e.g., Hinton and Upton, 1991; Hanchar and Hoskin, 2003). The investigation of the chondrite-normalized REE patterns is of petrological significance and the abundance and ratios of these trace elements are potentially useful in distinguishing zircon grains from different sources (e.g., Heaman et al., 1990).

Due to its resilient nature, zircon is a stable mineral in many geologic environments on Earth over very long periods of time, and therefore can be found in many igneous, metamorphic and

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sedimentary rocks and is particularly common in plutonic rocks (i.e., rocks of intermediate to Si-saturated composition), but also found in lunar rocks, several meteorite groups and tektites as discussed below. However, zircon is not ubiquitous as it does not occur in every rock type (e.g., Belousova et al., 2002), which also applies for meteoritic rocks and is demonstrated in this study.

The occurrence of zircon in extraterrestrial material was first described by Laspeyres in 1897, who discovered zircon grains in insoluble residues of the Toluca type IA iron meteorite. The author reported an acid dissolution separation of ~73 μg of zircon from 585 g of Toluca "Rostrinde" (rust), produced by corrosion in the humid storage environment of the Mineralogical Museum in Bonn, Germany. In 1964, Marvin and Klein investigated a specimen of the Toluca iron again, cutting away the weathered portions of the meteorite and working with troilite nodules from the interior. They dissolved several troilite nodules in dilute HCl and obtained two minute crystals of zircon which were euhedral, colorless, and clear except for a few inclusions, and therefore similar to those described by Laspeyres. In 1964, Marvin and Klein also reported on zircon grains, found in the insoluble residues of two uncrushed bulk specimens from the Vaca Muerta mesosiderite. A total mass of about 2 mg of zircon were obtained from 125 g of the host mesosiderite. From that time on, zircon and other Zr-bearing phases were found to be widely distributed accessory phases in several meteorite groups, spanning from undifferentiated to differentiated meteorite groups, as discussed in the following chapter.

Despite their rarity, due to their applicability as a reliable geochronological tool and ability for the uptake of REEs, zircon and other Zr-bearing phases in meteorites have been studied for several decades. With the development of high spatial resolution analytical techniques, such as secondary ion mass spectrometry (SIMS), meteoritic zircon in particular became increasingly suitable for isotopic and chemical analysis (e.g., Ireland and Wlotzka, 1992; Misawa et al., 2005; King et al., 2005; Srinivasan et al., 2007; Nemchin et al., 2009, 2010; Roszjar et al., 2011, 2012, in preparation). Such measurements are useful to evaluate the genesis (i.e., formation ages and conditions), and evolutionary history of meteorites in a petrological and geochemical context, as well as to constrain the thermal history of their parent bodies (Moon, Mars, and several asteroids from the asteroid belt). The aim of this study is to provide an overview on the distribution and chemical fingerprint of meteoritic zircon with the study of their REE systematics in particular.

2. Analytical techniques and sample materials

Petrography and mineral–chemical composition of selected sample materials were studied in thin- and thick sections using an optical Zeiss microscope and a JEOL 6610-LV scanning electron microprobe (SEM) equipped with energy dispersive spectrometers (EDS; INCA; Oxford Instruments) at the Interdisciplinary Center for Electron Microscopy and Microanalysis (ICEM) at the Westfälische Wilhelms-Universität Münster. Qualitative analyses for phase identification were carried out using an acceleration voltage of 20 kV and a beam current of 15 nA. High contrast, low brightness back-scattered electron (BSE) imaging was used for systematic localization of individual zircon grains mainly in basaltic eucrite samples and one ordinary chondrite. Back-scattered electron and cathodoluminescence (CL) imaging, using Oxford-detector systems, were used for petrographical characterization of zircon grains. Investigated samples include 10 basaltic eucrite finds: Dar al Gani (DaG) 276 and 391, Dhofar (Dho) 182, Hammadah al Hamra (HaH) 286, Northwest Africa (NWA) 1908, 2550, 4523, 5073 and 5356, Sahara (Sah) 98110, and one fall: Millbillillie, as well as the Barwell L5 ordinary chondrite. The eucrite samples are brecciated with shock-stages ranging from S2 (DaG 391, Dho 182, Sah 98110, NWA 1908, 2550), to S4 (HaH 286) according to the classification scheme defined for chondrites (Stöffler et al., 1991), and are metamorphosed to varying degrees, except for the unbrecciated and unmetamorphosed NWA 5073 sample (Roszjar et al., 2009, 2011).

The BSE imaging of these samples allowed selection of appropriate grains for subsequent ion microprobe analyses, which are of sufficient size (≥8 μm), mostly free of cracks and inclusions, and representative of the entire zircon population in selected eucrite samples in terms of grain shape and textural context. Some examples are given in Fig. 1. Quantitative analyses of zircon chemical compositions were obtained by wavelength dispersive analysis, using a JEOL JXA 8900 Superprobe electron probe micro analyzer (EPMA, ICEM facility) operated at an acceleration voltage of 15 kV and beam current of 15 nA. Natural and synthetic standards of well-known compositions were used. Matrix corrections were made according to the $\Phi\rho(z)$ procedure of Armstrong (1991). The same spots on selected zircon grains that were investigated by optical microscopy, SEM, and EPMA were subsequently analyzed for their REE concentrations using the ion microprobe. Details of major- and minor element concentrations, and crystal sizes are given in Table 1.

Rare earth element concentrations of individual zircon grains were determined using a large-radius magnetic sector multicollector Cameca IMS-1280 ion microprobe located at the Swedish Museum of Natural History (NRM, NORDSIM facility), Stockholm. An aperture-illuminated, slightly elliptical primary beam of approximately 10 μm in size was used to analyze the zircon grains. The field of view controlling the area of the sample from which ions were admitted to the mass spectrometer was set by adjusting the field aperture in the secondary ion optics to limit measured secondary ions only to those emitted from a sampled square area (typically ~7 × 7 μm) within the sputtered spot, which is smaller (in some cases considerably smaller) than any of the analyzed zircon grains. Once the field aperture size was set, small (~1 μm) stepped sample stage movements were used while observing the scanning ion image of the $^{90}Zr^{16}O_2$ mass to ensure that the field aperture was evenly illuminated by a zircon matrix species.

A hybrid mono-multicollector method was used for quantitive analyses of Dho 182, NWA 5073 (Zr-6-8 only), and NWA 5356 zircon grains, closely following the procedure described in Whitehouse (2004) with the exception that due to the detector configuration of the instrument at the time of these analyses, Ce had to be determined as part of the mono-collection sequence, while La, Pr, Nd, Sm, and Eu were determined simultaneously in the multicollector array. In this hybrid mode, a mass resolution of ~5000 ($M/\Delta M$) was applied to eliminate potential interfering masses in the multicollector measurements of La, Pr, Nd, Sm and Eu, while analyses of the other REE (including Ce) used a low mass resolution ($M/\Delta M \sim 1500$) combined with energy filtering to eliminate molecular interferences. All remaining zircon grains were analyzed following the method described in Whitehouse and Platt (2003) using a low mass resolution ($M/\Delta M \sim 1500$) monocollection mode for all species. In some cases, grains were observed to be partially or entirely sputtered away during analysis and so for later analyses, the abundant middle to heavy (M–H) REE only were measured (i.e., Gd, Dy, Er, and Yb) in order to shorten the analysis time and preserve sample material.

Isobaric interferences on ^{139}La, ^{140}Ce, and ^{141}Pr occur in zircon as a result of various ZrSiO species and require mass resolution >~5000 ($M/\Delta M$) to be resolved. These were monitored at mass 134 ($^{90}Zr^{28}Si^{16}O$) and appropriate corrections using the isotopic composition of Zr and Si (O isotope corrections are trivial at the achieved precision level) were applied to ^{140}Ce for all analyses and, in the monocollection analyses only, to ^{139}La and ^{141}Pr. Additionally, isobaric interferences on some of the LREE could be generated if the ion beam overlaps onto other mineral phases (either laterally or by sampling an inclusion) or depth-profiles into the substrate.

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