Mineral chemistry of angrite NWA 4590, and its potential use for inter-calibration of isotopic chronometers.
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Introduction: Besides their role as the probes to the early Solar System processes, angrites can serve as reference samples for inter-calibration of isotopic chronometers. Rich and diverse mineralogy and good preservation of angrites enables their precise and accurate dating with many long-lived (^{235,238}U-^{232}Th-^{206,207,208}Pb, ^{176}Lu-^{176}Hf, ^{146,147}Sm-^{142,143}Nd, initial Sr) and short-lived (^{53}Mn-^{53}Cr, ^{26}Al-^{26}Mg, ^{60}Fe-^{60}Ni, ^{182}Hf-^{182}W, and potentially other) isotopic chronometers, and makes angrites suitable for linking timescales based on different decay schemes, verifying initial abundances of short-lived radionuclides in the early Solar System, and determining half-lives of long-lived radionuclides by age comparison.

The recently discovered angrite NWA 4590 is among the best candidates for these studies. It is a very fresh coarse-grained igneous cumulate rock composed of Al-Ti-rich clinopyroxene, anorthite, Ca-rich olivine with kirschsteinite exsolution, ulvöspinel, and accessory minerals [1, 2] including merrillite [3] and silico-apatite [4]. The Pb-Pb isochron for pyroxene yields the age of 4557.93±0.28 Ma (approximating crystallization age), whereas the Pb-Pb isochron for silico-apatite yields the timing of 4557.381±0.066 Ma for closure of Pb diffusion in silico-apatite [5]. Very fast cooling rate of 540±290 K/Ma, calculated from these ages and the difference in closure temperature for Pb diffusion between pyroxene and silico-apatite (assumed to be the same as in apatite), makes chronometer comparisons based on analysis of this meteorite rather insensitive to the differences in closure temperatures of diffusion of various parent and daughter elements.

Here we report trace element concentrations in rock-forming and accessory minerals from NWA 4590, and use these data to evaluate the possibility of using these minerals for chronometer inter-calibration.

Methods: Grains of olivine (± kirschteinite), anorthitic plagioclase, Fe-rich (dark-colored) and Mg-rich (light-colored) varieties of pyroxene, ulvöspinel, merrillite and silico-apatite were hand-picked from a coarsely crushed meteorite, mounted in epoxy resin, and analyzed using EDS-SEM or electron microprobe to confirm their identity. Concentrations of trace elements were determined by laser ablation with a Lambda Physik 193 nm wavelength ArF laser connected to an Agilent 7500S ICP-MS through a high-efficiency small-volume sample cell and signal smoother to remove the effects of ablating with a pulsed laser. The sample was ablated in a He atmosphere using a ca. 50 μm laser spot. The concentrations are calculated relative to the NIST SRM 613 sample, with additional accuracy monitoring using NIST SRM 611 and SRM 615. More details about the technique are presented in [6] and references therein. The technique of U-Pb isotope dilution analysis is described in the companion abstract [5].

U-Th-Pb systems: Pyroxene and silico-apatite are very well suited for U-Pb dating [5]. High concentration of U (~8 ppm) and Th (~64 ppm) in merrillite suggests that it can also be a useful U-Th-Pb geochronometer mineral. Contributions of radiogenic Pb from phosphate minerals to analyses of silicate minerals that have much lower U and radiogenic Pb can be recognized using model ^{232}Th/^{238}U ratios calculated from Pb isotopic composition (Fig. 1): merrillite has ^{232}Th/^{238}U≈8, whereas silico-apatite has ^{232}Th/^{238}U between 2.5 and 2.8.

REE and Sm-Nd systems: Rare earth distributions in olivine, pyroxene, and phosphate minerals are shown in Fig. 2. The Sm/Nd ratios in olivine and pyroxene are substantially higher than the chondritic values. The Sm/Nd ratios in pyroxene broadly correlate with Mg (or Fe) abundances, therefore it may be possible to extend the spread of the Sm-Nd isochrons by picking Mg-rich and Fe-rich pyroxene separately. Phosphate minerals have high REE abundances and relatively uniform Sm/Nd ratios below chondritic value. Plagioclase and ulvöspinel have very low REE abundances (except Eu in plagioclase), and are unlikely to be useful for constructing precise Sm-Nd isochrons.

Lu-Hf system: Both phosphate minerals are rich in Lu (~130 times chondritic in silico-apatite, and ~220 times chondritic in merrillite), and are likely to be suitable for Lu-Hf dating. The Lu/Hf ratio in silico-apatite is about 50 times higher than chondritic. The ratio in merrillite could not be measured because Hf is below the detection limit of our laser ablation technique. The difference in Zr concentration suggests that the Lu/Hf ratio in merrillite should be ~100-200 times higher than in silico-apatite. Ulvöspinel, on the contrary, has very low REE abundances but elevated Zr and Hf (about 100 ppm, and 1 ppm, respectively), and may be suitable for determination of initial Hf isotopic ratio.

Initial Sr system: NWA 4590, like other angrites, is depleted in Rb. Several minerals rich in Sr and poor in Rb: plagioclase, pyroxene, merrillite, and silico-apatite, are suitable for initial Sr determinations.

Al-Mg system: Plagioclase has extremely high Al/Mg about 12,000 times higher than chondritic. However, it is likely that NWA 4590 is too young for ^{26}Al-^{26}Mg dating.

Mn-Cr system: Olivine and kirschteinite, with Mn/Cr ratios of about 1200 and 1600 times chondritic, are the principal Mn-Cr geochronometer minerals. The low-Mn/Cr mineral (0.27 times chondritic) is Mg-rich pyroxene, whereas Fe-rich pyroxene and ulvöspinel have intermediate Mn/Cr about 2.5-2.8 times chondritic. Hand-picking of minerals would be, therefore, a more efficient method of extending span of the isochron in the low Mn/Cr range, than partial dissolution of whole rock.

Fe-Ni system: Most minerals in this rock: olivine ± kirschteinite, pyroxene, ulvöspinel and silico-apatite, have high Fe/Ni ratio between 1,000 and 3,5000 times chondritic, and would be suitable for constricting a precise mineral isochron.

Hf-W system: Concentration of W in silicate minerals is below detection limit of our technique, but elevated concentration of Hf of about 40 times chondritic supports the choice of pyroxene as the main high-Hf/W geochronometer mineral in angrite dating [7, 8]. In contrast to the silicate minerals, both phosphate minerals and ulvöspinel are enriched in W (50-500 times chondritic) and have Hf/W of 0.15 times chondritic ratio or lower. These minerals, which are much more abundant and easier to separate than the metal, would be useful for constraining the initial ratio.

Nb-Zr system: The principal carrier of Nb is ulvöspinel, with the concentration about 600 times higher than in CI chondrites, and elevated Nb/Zr ratio of 28±10 times chondritic. Silico-apatite and pyroxene also contain measurable quantities of Nb and Zr, and with their Nb/Zr ratios of ~1 times chondritic and 0.04-0.06 times chondritic, respectively, would be useful for constraining the low-Nb/Zr end of the mineral isochron.

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References: [1] Irving A. J. et al. (2006) EOS, Trans. AGU 87, Fall Mtg. Suppl., Abstract #P51E-1245. [2] Kuehner S. M. and Irving A. J., (2007) 38th *LPS*, Abstract # 1522. [3] Sanborn M. E. and Wadhwa M. (2010) 40th *LPS*, Abstract # 1345. [4] Mikouchi T. et al. (2011) 42nd *LPS*. [5] Amelin Y., Kaltenbach A. and Stirling C. H. (2011) 42nd *LPS*. [6] Ambrose W. et al. (2009) *Journal of Archaeological Science* 36, 607–615. [7] Markowski A. et al. (2007) *EPSL* 262, 214–229. [8] Kleine T. et al. (2008) 39th *LPS*, Abstract # 2369.

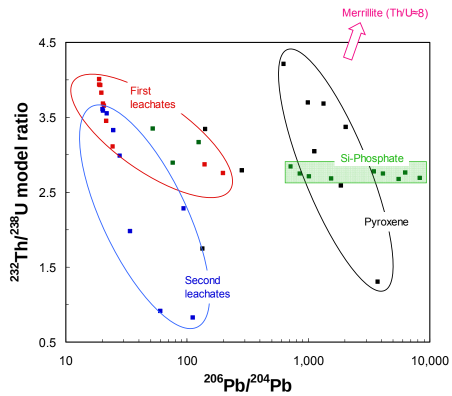

Fig. 1. Model ^{232}Th/^{238}U ratios (calculated from radiogenic ^{208}Pb/^{206}Pb ratio and the age) for minerals from NWA 4590.

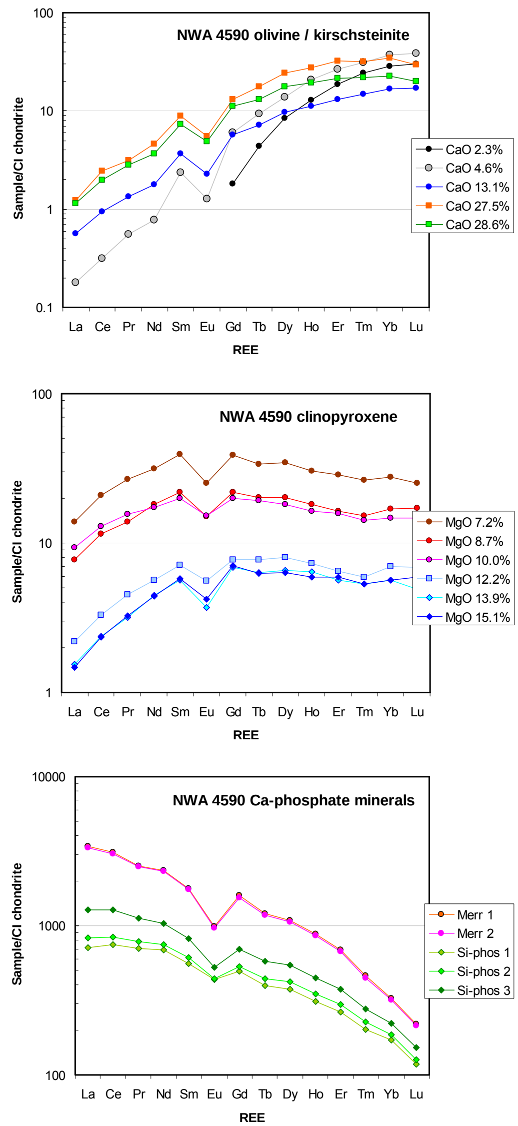

Fig.2. Rare Earth Element patterns in minerals from the angrite NWA 4590, normalized to abundances in CI chondrites.