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Invited review

Angrites, a small but diverse suite of ancient, silica-undersaturated volcanic-plutonic mafic meteorites, and the history of their parent asteroid

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ABSTRACT

Angrites are medium- to coarse-grained (up to 2-3 mm), unbrecciated and substantially unshocked igneous rocks of roughly basaltic composition. They are the most alkali-depleted basalts in the Solar System, but are not very depleted in moderately volatile elements such as Br, Se, S, Zn, In and Cd, and are relatively enriched in refractory elements such as Ca and Ti. They have uniform oxygen isotopic compositions and form a mass fractionation line on a Δ^{17} O vs. δ^{18} O diagram of Δ^{17} O = -0.072 ± 0.007 that sets them apart from other extraterrestrial basalts such as the HEDs. They consist of major Al-Ti-bearing diopside-hedenbergite (formerly called fassaite), calcic olivine, and anorthite. Minor and accessory phases include kirschsteinite, spinel, ulvöspinel, metallic Fe,Ni, troilite, titanomagnetite, whitlockite, ilmenite, and very rare carbonates, celsian, rhönite, and baddeleyite. On the basis of texture and mineralogical composition, they are divided into plutonic (5 members, +8 paired specimens) and volcanic (quenched) (6 members) angrites. Plutonic angrites have hypidiomorphic to granular and cumulate textures and contain nearly equilibrated, homogeneous minerals, whereas volcanic angrites have quench textures and consist of highly zoned minerals. These differences are the result of their different cooling rates: plutonic angrites cooled at model dependent rates of ~303-323 K/a or ~274.6-275.4 K/a (burial depths 14-17 or 68–75 m, respectively), whereas volcanic angrites cooled at \sim 280–286 K/h in the temperature range of 1573-1273 K, implying a burial depth of <0.5 m. The angrites are amongst the oldest basaltic rocks in the Solar System, and Pb-Pb ages show that the slowly cooled plutonic angrites have younger ages ranging from \sim 4558.86 \pm 0.30 to 4557.65 \pm 0.13 Ma, and the more quickly cooled volcanic angrites have older ages ranging from 4564.18 ± 0.14 to 4563.8 ± 0.4 Ma. While it has been suggested that the planet Mercury may be the source of the angrites, overwhelming evidence has been accumulated that they are fragments of a differentiated asteroid, probably >100 km in radius and with a metal core which, based on $^{182}\text{Hf-}^{182}\text{W}$ systematics, formed within $\sim\!2\,\text{Ma}$ of CAI formation. The origin and source lithologies of these fascinating rocks have been the topics of intense debates, and no consensus has yet been reached. However, the angrites are clearly igneous rocks and not impact melt-rocks or nebular condensates.

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1. Introduction

The first comprehensive and multidisciplinary study of an angrite, the type meteorite that fell into the Bay of Angra dos Reis, Brazil, at about 5:00 a.m. in the latter half of January, 1869 (Ludwig and Tschermak, 1887), was carried out by the ADORABLES (1976), the members of the Angra dos Reis Consortium, of the only angrite known at the time (Keil, 1977; Brett et al., 1977; Dowty, 1977; Hazen and Finger, 1977; Lugmair and Marti, 1977; Ma et al., 1977; Mao et al., 1977; Prinz et al., 1977; Störzer and Pellas, 1977; Wasserburg et al., 1977). The fall had been observed by a local judge and the meteorite weighing ~1500 g was recovered by a diver from

a depth of 2 m one day after the fall, but only ~ 150 g seem to be preserved. Since then, nine additional angrites have been discovered in hot and cold deserts and one in Argentina (Table 1). These new discoveries have much contributed to a better understanding of the mineralogy, petrology and geochemistry of these enigmatic but fascinating rocks, and of the volcanic-plutonic history of their parent body very early in the history of the Solar System (e.g., Mittlefehldt and Lindstrom, 1990a; Mittlefehldt et al., 1998, 2002).

The angrites are important mafic volcanic-plutonic rocks that provide critical data for understanding the early evolution of a unique differentiated asteroid. They are the most alkali-depleted rocks in the Solar System (e.g., Warren and Kallemeyn, 1995; Warren et al., 1995) and, unlike the HEDs and aubrites, they show little evidence for shock and impact brecciation. Most importantly, they have preserved a record of some of the earliest volcanic activity in the Solar System ~4564 Ma ago and only ~4 Ma after formation

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Table 1Listing of plutonic and volcanic angrites, their date of fall/find, location, and mass.

| Plutonic angrites | Date of fall/find | Location | Mass (g) |
|-------------------------------------|------------------------------|-------------------------------|-------------------------|
| Angra dos Reis (stone) ^a | Latter half of January, 1869 | Bay of Angra dos Reis, Brazil | ~1500 |
| LEW 86010 | 1986 | Lewis Cliff, Antarctica | 6.9 |
| NWA 2999 ^b | August 2004, 2005 | Morocco or Algeria | 392°, 2400 ^d |
| NWA 3158 ^b | August 2004 | Northwest Africa | 681 |
| NWA 3164 ^b | August, 2004, 2005 | Morocco or Algeria | 928 |
| NWA 4569 ^b | 2005 | Northwest Africa | 484 |
| NWA 4662 ^b | 2006 | Northwest Africa | 60 |
| NWA 4877 ^b | 2007 | Northwest Africa | 1000 |
| NWA 4931 ^b | 2007 | Northwest Africa | 2140 |
| NWA 5167 ^b | 2007 | Morocco | 859 |
| NWA 6291 ^b | 2010 | Northwest Africa | 250 |
| NWA 4590 | 2006 | Bechar, Algeria | 213 |
| NWA 4801 | 2007 | Algeria | 252 |
| Volcanic angrites | | | |
| Asuka 881371 | 1988 | Antarctica | 11.3 |
| D'Orbigny | July, 1979 | Argentina | 16550 |
| LEW 87051 | 1987 | Lewis Cliff, Antarctica | 0.6 |
| NWA 1296 | Spring, 2001 | Morocco, purchased in Bouarfa | 810 |
| NWA 1670 | Purchased 2003 | Northwest Africa | 30.6 |
| Sahara 99555 | 1999 | Sahara | 2710 |

- ^a Observed fall.
- ^b Paired.
- ^c Bunch and Wittke (2008).
- d Irving et al. (2005).

of the first solids in the Solar System, the CAIs, and they provide "pivotal reference points for early Solar System chronology" (e.g., Kleine et al., 2012).

An unfortunate situation exists with published literature on angrites, in that many critical data and descriptions have only been released in the form of abstracts. Thus, some of the information on angrites is, unfortunately, contained in documents that have not gone through the scrutiny of peer review.

2. Mineralogy and petrology

Angrites are medium- to coarse-grained (up to 2-3 mm), unbrecciated and essentially unshocked mafic to basaltic (Table 10) igneous crustal rocks (Fig. 1) and have Fe isotopic (∂^{56} Fe) composition heavier than chondrites and similar to terrestrial basalts (Wang et al., 2012). On the basis of their textures and mineralogies, they have been divided into plutonic and volcanic (quenched) angrites, a classification I will follow in this paper (e.g., Irving et al., 2005; Kuehner et al., 2006; Sanborn and Wadhwa, 2010) (Table 1). [Note that Jambon et al. (2008, 2012), divided angrites into picritic rocks (those consisting of a mixture of angritic melt and olivine xenocrysts (NWA 1670, LEW 87051, Asuka 881371, NWA 1296), angrite melts (LEW 86010, D'Orbigny), and cumulates (Angra dos Reis); Jambon et al., 2012 referred to NWA 2999 and its pairs as chimerolites.] Kuehner et al. (2006) point out that rocks such as NWA 2999, LEW 86010 and Angra dos Reis (the plutonic angrites) are possibly thermally annealed formerly brecciated ultramafic rocks (and probably ancient regolith), although they do not provide any strong evidence for this proposition, and Treiman (1989) suggests that Angra dos Reis is a porphyritic igneous rock, not a cumulate (Prinz et al., 1977). The bulk (3.38, 3.24) and grain densities $(3.48, 3.37, in g cm^{-3})$ of two plutonic angrites, NWA 4590 and NWA 4801, have been determined (Macke et al., 2011). Thus, their porosities, not unexpected for igneous rocks, are relatively low at 6.79 and 5.66%, respectively.

The plutonic angrites have nearly equilibrated mineral constituents with little, if any, zoning, whereas the volcanic angrites are characterized by disequilibrium, highly zoned assemblages (e.g., Figs. 1 and 2). This is the result of their different cooling histories: the plutonic angrites cooled slower than the volcanic angrites. The

earliest rough cooling rate estimate of >70 K/Ma is based on ²⁴⁴Pu fission tracks and ²⁴⁴Pu-fission Xe in the plutonic angrite Angra dos Reis (Störzer and Pellas, 1977). However, later measurements are much more accurate: Olivine in the plutonic angrite LEW 86010, for example, contains abundant exsolution lamellae of kirschsteinite, with two sets of lamellae symmetrically related and parallel to (031) and (031) (Mikouchi et al., 1993, 1995a). Compositional diffusion gradients between lamellae and host allow model-dependent cooling rates and burial depths of the rock to be estimated, based on the diffusion of Ca in olivine. McKay et al. (1998) state that "most of the exsolution in LEW 86010 took place below 1273 K", and determination of the cooling rates requires uncertain extrapolations of the diffusion rates of Ca in olivine measured at temperatures above 1373 K (e.g., Jurewicz and Watson, 1988) to the lower temperatures. The cooling rates determined by this method vary between 303 and 323 K/a (burial depth 14–17 m) and 274.6–275.4 K/a (burial depth 68-75 m), depending upon assumptions on the Ca diffusion rates (McKay et al., 1989, 1993, 1998). However, I should note that these cooling rates and burial depths are hardly consistent with a true "plutonic" origin of these rocks and instead may suggest an origin in near-surface dikes, shallow intrusions or thick or ponded lava flows near the surface of the APB. Also, Markowski et al. (2006a) confirmed with Wisotopes that the plutonic angrite NWA 2999 belongs to the group of "slowly cooled" angrites. Quitte et al. (2007) showed that for the plutonic angrite NWA 2999, the ⁶⁰Fe-⁶⁰Ni system closed more than 8.3 Ma after the beginning of the solar system, which is compatible with ¹⁸²Hf-¹⁸²W data of Markowski et al. (2006a,b), and also suggests relatively "slow" cooling when compared to the volcanic angrites. Note that Amelin et al. (2011b) calculated from the Pb-Pb ages for pyroxene and silico-apatite and the difference in closure temperature for Pb diffusion in those minerals what they call "a very fast cooling rate" of 540 ± 290 K/Ma for the plutonic angrite NWA 4590. This slow cooling rate of \sim 0.00054 K/a is in clear conflict with the much faster rates obtained by the authors listed above.

On the other hand, initial studies by Mikouchi et al. (1995c) of the zoning profiles in olivine of the volcanic angrite LEW 87051 yielded a rough cooling rate of faster than 1273 K/a, which would imply an approximate burial depth of \sim 2 m in solid rock or \sim 0.1 m in regolith. Also, while they could not quantify the exact cooling rates, Floss et al. (2003) point out that trace

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