

OXYGEN ISOTOPE EVIDENCE FOR THE EXTRA-TERRESTRIAL ORIGIN OF THE FIRST NATURAL QUASICRYSTAL. Y. Guan¹, L. Bindi^{2,3}, J. M. Eiler¹, L. Hollister⁴, G. J. MacPherson⁵, P. J. Steinhart^{6,7} and N. Yao⁸, ¹Division of Geological and Planetary Sciences, Caltech, Pasadena, CA 91125 USA (yubin@gps.caltech.edu). ²Museo di Storia Naturale, Sezione di Mineralogia, Università degli Studi di Firenze; ³CNR-Istituto di Geoscienze e Georisorse, Sezione di Firenze, Firenze, I-50121 Italy. ⁴Department of Geoscience, Princeton University, Princeton, NJ 08544 USA. ⁵Division of Meteorites, Smithsonian Institution, Washington DC, 20013 USA. ⁶Princeton Center for Theoretical Science, Princeton University, Princeton, NJ 08544 USA. ⁷Department of Physics, Princeton University, Princeton, NJ 08544 USA. ⁸Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, NJ 08544, USA.

Introduction: Quasicrystals are solids with structures that are characterized by rotational symmetries forbidden to crystals, including five-fold symmetry in the plane and icosahedral symmetry in three dimensions [1]. For decades, the only known examples of quasicrystals had been synthetic materials produced by mixing precise ratios of selected elemental components in the liquid and quenching under controlled conditions ranging from rapid to moderately slow [2,3], until Bindi *et al.* discovered the first natural quasicrystal [4]. In this report we present oxygen isotopic evidence that this naturally occurring quasicrystal is part of a carbonaceous chondrite, presumably formed in the early solar system about 4.5 Ga ago.

The Natural Quasicrystal and Hosting Sample:

The quasicrystal, an alloy of Al, Cu, and Fe, was discovered in a rock sample found in the Koryak Mountains in Russia. Its quasicrystalline nature was established by x-ray diffraction, by transmission electron microscopy (TEM) diffraction, and by matching the stoichiometry with known synthetic quasicrystals [4]. The quasicrystal grains show nearly perfect icosahedral symmetry and quasiperiodic translational order. The measured composition of the grains, Al₆₃Cu₂₄Fe₁₃, agrees with the stoichiometry of a known quasicrystal synthesized in the laboratory.

The quasicrystal occurs as micrometer-sized grains in a complex assemblage that includes silicate (diopside, forsterite), oxide (spinel) and other metallic [khatyrkite (CuAl₂), cupalite (CuAl)] crystalline phases [4]. The olivine grains are near end-member forsterite (atomic Mg/(Fe+Mg) up to 99%) and the pyroxene grains are near end-member diopside (atomic Mg/(Fe+Mg) up to 99%). Evidence of zoning in P, Cr, and Ni was found in some of the forsterite grains.

A single olivine (~20x30 μm) grain mount and numerous finer grains (<10 μm) from powder of the quasicrystal-bearing sample were selected for O isotopic analyses in two analytical sessions.

Analytical Techniques: The large single olivine grain was measured with the Cameca ims 7f-Geo SIMS at Caltech, with a +10 keV Cs⁺ primary beam of ~10 μm and ~0.2 nA. Secondary ions of -10 keV were

collected with either a Faraday cup (FC) (¹⁶O⁻) or an electron multiplier (EM) (¹⁷O⁻ and ¹⁸O⁻) at a mass resolving power of ~5000. Instrumental mass fractionation (IMF) was corrected by measuring the San Carlos olivine standard. Analytical errors of each individual run, taking into account the variations of repeated measurement of the standard, are ~±1‰ (1σ) for both δ¹⁷O and δ¹⁸O.

The O isotopes of fine grains of the powdered quasicrystal-bearing sample were measured with the Cameca NanoSIMS 50L at Caltech. A +8 keV Cs⁺ primary beam of 8-12 pA was rastering over a 3x3 μm area. Secondary ions (¹⁶O⁻, ¹⁷O⁻, and ¹⁸O⁻) of -8 keV were simultaneously measured in multicollection mode with the Hamamatsu EMs. The pulse height distribution (PHD) of each EMs, especially the one for ¹⁶O⁻, was closely monitored for signs of drift in EM gain. IMF was corrected by repeated measurements of three different standards: San Carlos olivine, Eagle Station olivine, and Burma spinel. The errors of δ¹⁷O and δ¹⁸O for each individual run, taking into account the variation from repeated standard measurements, were ~±(3.5)‰ and ~±1.5‰ (1σ), respectively. The larger errors of δ¹⁷O were mostly derived from low counting rates of ¹⁷O⁻. This combination of both instruments and methods permitted us to make a relatively confident analysis of the single large olivine grain available for this study, as well as a large number of less precise analyses of the more numerous and diverse small grains.

Results: The O isotopic compositions of pyroxene, spinel, nepheline and olivine from the quasicrystal-bearing sample are plotted in the Fig. 1. Also plotted in the same figure are the data for different standards. All the sample data fall on the carbonaceous chondrite anhydrous minerals (CCAM) line. The spinel grain is highly ¹⁶O-enriched (δ¹⁷O ~ δ¹⁸O ~-40‰), which is typical for CAI spinel. Both the large single olivine measured with the 7f-Geo and small olivine grains with the NanoSIMS 50L have δ¹⁷O and δ¹⁸O values at ~-10‰ and ~-5‰, respectively. The O isotopic composition of one nepheline grain overlaps with that of the olivine grains. Many CV and CO chondrites con-

tain olivine or altered minerals with similar O isotopic values [5]. Relatively heavier O isotopic compositions were exhibited by the pyroxene grain, with $\delta^{17}\text{O} \sim -2\text{‰}$ and $\delta^{18}\text{O} \sim 10\text{‰}$. Unlike the spinel, the pyroxene grain could not be a primary CAI component. Instead, its heavy $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values probably indicate isotopic exchange during late metamorphism. In addition, SIMS crater images indicate mixing with surrounding material (matrix?) for some of the NanoSIMS measurements.

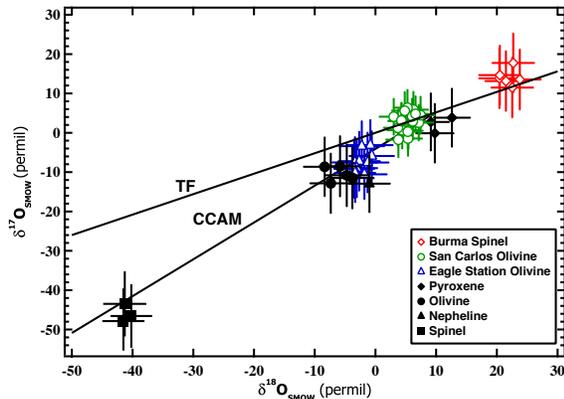


Figure 1. Oxygen isotope of standards (Burma spinel, San Carlos and Eagle Station olivines) and individual minerals (pyroxene, nepheline, olivine, and spinel) from the quasicrystal-bearing sample, based on NanoSIMS ion microprobe measurements. TF – terrestrial fraction line; CCAM -- carbonaceous chondrite anhydrous mineral line. Error bars are 2σ .

Discussion and Conclusions: Serious consideration has been given to the possibility that the origin of the rock is anthropogenic, but the silicate and oxide properties above, along with the absence of glass, bubbles, myrmekitic textures, and other features typical of anthropogenic processes, do not support this hypothesis. The SIMS measurements we present document a range of oxygen isotope compositions closely similar to the CCAM trend — convincing evidence that the diverse assemblage of silicates and oxides in the quasicrystal-bearing rock sample are extra-terrestrial, consistent with high temperature refractory minerals formed in the early solar system. Finally, the large olivine crystal analyzed with the 7f-Geo is tightly intergrown with quasicrystal grains, establishing an apparent textural equilibrium.

The quasicrystalline phase found in the meteoritic sample matches in structure and stoichiometry with one first synthesized in the laboratory by slow quench methods in the 1980s [6,7]. Our results push the age of the oldest known example of this phase back to *ca.* 4.5 Ga (presuming the sample is similar in age to all the

other known primitive meteorites). The synthetic $\text{Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$ samples were prepared at standard pressure from a liquid mix of metal alloys only and cooled under carefully controlled conditions. The stability of this phase was studied for a range of compositions and temperatures [7]; the range of stable compositions was found to narrow as the temperature decreases, centering around the composition measured in our natural sample, all the way down to the temperature where the solid finally falls out of equilibrium. This trend led some to suggest that quasicrystals are inherently unstable at low temperatures and generically difficult to form except under carefully controlled laboratory conditions. The occurrence in a meteoritic sample demonstrates that the same quasicrystal phase can form in a complex, inhomogeneous medium and remain stable over cosmic timescales. From the perspective of condensed matter physics, this observation lends support to the original proposal [4] suggesting that quasicrystals can be as stable as crystals, and, therefore, have equal footing as stable forms of solid matter.

In addition to the quasicrystal grains, the meteoritic components exhibits a combination of other unique, puzzling characteristics: (i) metallic aluminum alloys, presumably indicating extremely reducing conditions; (ii) interfaces between metallic and oxide phases with sharp boundaries and no significant reactions; (iii) highly forsteritic and ^{18}O and ^{17}O depleted olivine. Fitting these clues together in a consistent theory of formation and evolution of the meteoritic sample is the subject of an ongoing investigation. In addition, the ^{26}Al - ^{26}Mg isotopic systematics of the quasicrystal are investigated with the NanoSIMS at Caltech.

References: [1] Levine D. and Steinhardt P. J. (1984) *Phys. Rev. Lett.* 53, 2477-80. [2] Shechtman, D. et al. (1984) *Phys. Rev. Lett.* 53, 1951-1954. [3] Janot, C. (1994) *Quasicrystals: a primer*, Oxford U. Press, Oxford. [4] Bindi, L. et al. (2009) *Science* 324, 1306-1309. [5] Clayton R. N. (2005) In *Meteorites, Comets, and Planets*, ed. by Davis A. M., Elsevier, 129-142. [6] Tsai, A. P. et al. (1987) *Jap. J. Appl. Phys.* 26, L1505. [7] Bancel P. A. (1991) In *Quasicrystals: The State of the Art*, ed. by DiVincenzo D. and Steinhardt P. J., World Scientific, 17-56.