Earth and Planetary Science Letters 319-320 (2012) 251–258

Contents lists available at SciVerse ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

# Framboidal iron oxide: Chondrite-like material from the black mat, Murray Springs, Arizona

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ARTICLE INFO

*Article history:*
Received 26 January 2011
Received in revised form 16 November 2011
Accepted 22 November 2011
Available online 21 January 2012

Editor: L. Stixrude

*Keywords:*
Younger-Dryas
Clovis
meteorite
framboids
chondrite
black-mat

ABSTRACT

At the end of the Pleistocene a Younger Dryas "black mat" was deposited on top of the Pleistocene sediments in many parts of North America. A study of the magnetic fraction (~10,900 ± 50 B.P.) from the basal section of the black mat at Murray Springs, AZ revealed the presence of amorphous iron oxide framboids in a glassy iron-silica matrix. These framboids are very similar in appearance and chemistry to those reported from several types of carbonaceous chondrites. The glass contains iron, silicon, oxygen, vanadium and minor titanium, while the framboidal particles contain calcium as well. The major element chemistry of both the spherules and the glass matrix are consistent with the chemistry of material associated with meteorite impact sites and meteorites. Electron microscopy confirms that the glassy material is indeed amorphous, and also shows that what appear to be individual oxide particles are amorphous as well. The latter appears consistent with their overall morphology that, while euhedral, typically shows significant fracture. Based on these data, we argue that these particles are the product of a hypervelocity impact.
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## 1. Introduction

Approximately 13,000 years ago the landscape of North America was very different from that which exists today (e.g., Alley, 2007; Haynes, 2008). The Clovis people, identified in the archeological record by large, unique projectile points recovered throughout North America, were hunting mammoths and other megafauna that roamed the continent near the close of the Pleistocene (Haynes, 2008). After 12,900 years ago, however, neither these large mammals nor the material remains of the Clovis inhabitants appear in the geological or archeological records. Instead Folsom-style artifacts appear to have replaced Clovis (Haynes, 2008; Meltzer and Holliday, 2010). This coincides with a period in which the Younger Dryas (YD) climate was significantly colder than either the preceding late-Pleistocene (Allerød) or the succeeding early-Holocene (pre-Boreal). First recognized in pollen profiles from northern Europe, this cold reversal was named the Younger Dryas after fossil pollen of the dryas plant (*Dryas octopetala*), signifying a tundra flora, commonly found in its fossil pollen assemblages (Taylor and Lamorey, 1993). Radiocarbon ages for the YD vary, but dates of approximately 10,900 ± 50 B.P. for its beginning and 9800 ± 50 B.P. (12,900 years ago) for its end are reasonable (Fiedel, 2006; Haynes, 2008; Stuiver et al., 1995). There have been several hypotheses presented to explain these sudden changes in climate and human culture, as well as the late-Pleistocene extinction, and some are highly controversial (e.g., Alley, 2000, 2007; Bradley and England, 2008; Broecker, 2006; Broecker et al., 1985, 1989; Firestone et al., 2007; Gill et al., 2009; Kennett et al., 2008, 2009; Marlon et al., 2009; McManus et al., 2004; Pinter and Ishman, 2008). Nevertheless, it is clear that a major paleoenvironmental event occurred at ~12,900 years ago.

One of the geological markers often associated with the YD onset is a dark, organic-rich layer of clayey silt called the "black mat" (Firestone et al., 2007; Haynes, 2008; West and Goodyear, 2008). Black mats are found in two-thirds of the 97 geoarcheological sites that bridge the Pleistocene–Holocene transition (Haynes, 2008). Most black mats are paleosols, but some consist of a layer of organic material, varying in color from dark gray to black, considered to have been deposited under moist to wet conditions. Clovis artifacts and Pleistocene fauna are found directly beneath, but never within or above, the black mat (Haynes, 2008). Most YD-age black mats are dark gray to black due to relatively high organic carbon (0.05–8%) compared with strata above and below (Essene and Fisher, 1986; Lougheed and Mancuso, 1973). There are both younger and older black layers (Holliday and Meltzer, 2010), but they do not appear to be as common, pervasive or as widely distributed over North America

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doi:10.1016/j.epsl.2011.11.033

**Table 1**
Electron microprobe analysis of spherules and matrix of particles 1 and 2 from the >400 μm size magnetic fraction.

| Spherules-particle 1 | | | | | | | | | | | | | | | | | | Particle 2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | sph1 | sph2 | sph3 | sph4 | sph5 | sph6 | sph7 | sph8 | sph9 | sph10 | sph11 | sph12 | sph13 | sph14 | sph15 | avg | std | sph1 |
| $Na_2O$ | 0.13 | 0.27 | 0.34 | 0.38 | 0.23 | 0.18 | 0.05 | 0.14 | 0.25 | 0.26 | 0.51 | 0.15 | 0.20 | 0.12 | 0.14 | 0.22 | 0.12 | 0.19 |
| MgO | 0.35 | 0.24 | 0.23 | 0.29 | 0.28 | 0.26 | 0.28 | 0.25 | 0.31 | 0.35 | 0.32 | 0.40 | 0.25 | 0.32 | 0.28 | 0.30 | 0.05 | 0.41 |
| $Al_2O_3$ | 0.53 | 0.98 | 0.85 | 0.76 | 0.69 | 0.58 | 0.52 | 0.57 | 0.97 | 1.31 | 1.45 | 0.72 | 0.72 | 0.63 | 0.57 | 0.79 | 0.28 | 0.86 |
| $SiO_2$ | 6.47 | 8.50 | 7.18 | 7.34 | 6.81 | 7.01 | 6.34 | 6.96 | 6.98 | 8.69 | 10.35 | 7.83 | 6.20 | 6.53 | 6.57 | 7.32 | 1.12 | 10.19 |
| $SO_2$ | 0.42 | 0.42 | 0.54 | 0.45 | 0.58 | 0.38 | 0.49 | 0.91 | 0.36 | 0.22 | 0.35 | 0.37 | 1.26 | 1.35 | 1.88 | 0.67 | 0.47 | 0.16 |
| $K_2O$ | 0.01 | 0.08 | 0.03 | 0.04 | 0.04 | 0.02 | 0.02 | 0.01 | 0.02 | 0.04 | 0.07 | 0.01 | 0.03 | 0.01 | 0.02 | 0.03 | 0.02 | 0.03 |
| CaO | 1.67 | 1.96 | 1.69 | 1.63 | 1.60 | 1.82 | 1.73 | 1.80 | 1.98 | 1.99 | 2.03 | 2.19 | 1.61 | 1.61 | 1.55 | 1.79 | 0.20 | 3.08 |
| $TiO_2$ | 0.02 | 0.05 | 0.00 | 0.02 | 0.02 | 0.02 | 0.01 | 0.04 | 0.03 | 0.03 | 0.03 | 0.02 | 0.02 | 0.01 | 0.03 | 0.02 | 0.01 | 0.11 |
| $Cr_2O_3$ | 0.01 | 0.02 | 0.02 | 0.01 | 0.03 | 0.02 | 0.00 | 0.03 | 0.01 | 0.01 | 0.00 | 0.08 | 0.00 | 0.07 | 0.02 | 0.02 | 0.02 | 0.05 |
| MnO | 0.01 | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 | 0.02 | 0.00 | 0.02 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.02 | 0.00 |
| $Fe_2O_3$ | 81.63 | 67.10 | 78.69 | 75.84 | 82.56 | 80.18 | 75.22 | 79.28 | 76.69 | 73.97 | 71.51 | 79.59 | 80.43 | 82.16 | 82.35 | 77.81 | 4.44 | 71.24 |
| NiO | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.02 |
| $V_2O_3$ | 1.55 | 1.23 | 1.57 | 1.26 | 1.56 | 1.61 | 1.51 | 1.58 | 1.53 | 1.84 | 1.51 | 1.51 | 1.66 | 1.58 | 1.23 | 1.52 | 0.17 | 2.02 |
| Total | 92.80 | 80.85 | 91.14 | 88.01 | 94.43 | 92.08 | 86.18 | 91.60 | 89.15 | 88.76 | 88.14 | 92.88 | 92.37 | 94.38 | 94.63 | 90.49 | 3.73 | 88.36 |
| Atom percent | | | | | | | | | | | | | | | | | | |
| Na | 0.140 | 0.319 | 0.357 | 0.420 | 0.235 | 0.191 | 0.056 | 0.146 | 0.276 | 0.278 | 0.547 | 0.159 | 0.207 | 0.119 | 0.147 | 0.24 | 0.13 | 0.201 |
| Mg | 0.285 | 0.214 | 0.192 | 0.245 | 0.225 | 0.213 | 0.243 | 0.208 | 0.259 | 0.294 | 0.268 | 0.323 | 0.204 | 0.253 | 0.218 | 0.24 | 0.04 | 0.338 |
| Al | 0.340 | 0.701 | 0.552 | 0.507 | 0.435 | 0.373 | 0.355 | 0.370 | 0.640 | 0.861 | 0.944 | 0.459 | 0.460 | 0.397 | 0.358 | 0.52 | 0.19 | 0.559 |
| Si | 3.516 | 5.175 | 3.941 | 4.161 | 3.629 | 3.828 | 3.703 | 3.813 | 3.918 | 4.837 | 5.727 | 4.210 | 3.375 | 3.474 | 3.480 | 4.05 | 0.68 | 5.648 |
| S | 0.212 | 0.242 | 0.277 | 0.238 | 0.289 | 0.195 | 0.267 | 0.468 | 0.192 | 0.112 | 0.182 | 0.188 | 0.645 | 0.675 | 0.933 | 0.34 | 0.23 | 0.086 |
| K | 0.007 | 0.063 | 0.023 | 0.025 | 0.028 | 0.013 | 0.013 | 0.004 | 0.014 | 0.032 | 0.048 | 0.005 | 0.017 | 0.008 | 0.017 | 0.02 | 0.02 | 0.019 |
| Ca | 0.974 | 1.279 | 0.994 | 0.989 | 0.912 | 1.065 | 1.081 | 1.057 | 1.190 | 1.189 | 1.203 | 1.263 | 0.936 | 0.916 | 0.878 | 1.06 | 0.13 | 1.832 |
| Ti | 0.009 | 0.024 | 0.002 | 0.010 | 0.009 | 0.009 | 0.003 | 0.016 | 0.012 | 0.012 | 0.012 | 0.008 | 0.006 | 0.005 | 0.010 | 0.01 | 0.01 | 0.047 |
| Cr | 0.003 | 0.008 | 0.007 | 0.003 | 0.013 | 0.007 | 0.001 | 0.012 | 0.004 | 0.003 | 0.00 | 0.033 | 0.002 | 0.030 | 0.006 | 0.01 | 0.01 | 0.021 |
| Mn | 0.003 | 0.002 | 0.001 | 0.00 | 0.014 | 0.000 | 0.011 | 0.000 | 0.010 | 0.009 | 0.00 | 0.000 | 0.000 | 0.00 | 0.004 | 0.00 | 0.01 | 0.00 |
| Fe | 33.41 | 30.74 | 32.51 | 32.37 | 33.10 | 32.94 | 33.06 | 32.66 | 32.38 | 30.97 | 29.77 | 32.22 | 32.94 | 32.91 | 32.84 | 32.32 | 1.03 | 29.72 |
| Ni | 0.00 | 0.000 | 0.004 | 0.004 | 0.00 | 0.00 | 0.001 | 0.011 | 0.00 | 0.009 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.008 |
| V | 0.677 | 0.598 | 0.690 | 0.572 | 0.667 | 0.705 | 0.707 | 0.693 | 0.690 | 0.822 | 0.671 | 0.650 | 0.726 | 0.674 | 0.524 | 0.67 | 0.07 | 0.899 |

sph = spherules

| Matrix-particle 1 | | | | | | | | | | | | | | | | | Particle 2 Spherule 2 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | avg | std | 1 | 2 |
| $Na_2O$ | 0.07 | 0.14 | 0.19 | 0.11 | 0.17 | 0.16 | 0.19 | 0.40 | 0.15 | 1.02 | 0.75 | 0.78 | 0.45 | 0.16 | 0.14 | 0.33 | 0.30 | 0.00 | 0.00 |
| MgO | 0.56 | 0.45 | 0.60 | 0.51 | 0.52 | 0.61 | 1.43 | 0.69 | 0.51 | 1.56 | 1.61 | 1.00 | 0.93 | 0.62 | 0.48 | 0.80 | 0.41 | 0.00 | 0.00 |
| $Al_2O_3$ | 2.12 | 2.05 | 2.50 | 2.04 | 1.34 | 2.96 | 3.80 | 2.58 | 2.91 | 9.85 | 8.84 | 5.09 | 5.78 | 2.79 | 1.43 | 3.74 | 2.59 | 0.01 | 0.02 |
| $SiO_2$ | 14.48 | 13.04 | 14.42 | 12.41 | 12.54 | 13.94 | 17.68 | 14.87 | 15.75 | 33.62 | 24.21 | 17.45 | 18.74 | 15.24 | 12.30 | 16.71 | 5.61 | 96.20 | 97.37 |
| $SO_2$ | 0.12 | 0.07 | 0.10 | 0.06 | 0.11 | 0.07 | 0.10 | 0.14 | 0.06 | 0.41 | 0.62 | 0.78 | 0.33 | 0.08 | 0.22 | 0.22 | 0.22 | 0.01 | 0.00 |
| $K_2O$ | 0.05 | 0.07 | 0.12 | 0.10 | 0.01 | 0.26 | 0.31 | 0.15 | 0.18 | 2.52 | 0.75 | 0.48 | 0.50 | 0.20 | 0.02 | 0.38 | 0.63 | 0.01 | 0.06 |
| CaO | 3.45 | 2.86 | 3.28 | 3.23 | 4.19 | 3.18 | 3.27 | 3.44 | 2.52 | 3.23 | 4.30 | 5.70 | 3.49 | 3.38 | 4.17 | 3.58 | 0.76 | 0.06 | 0.07 |
| $TiO_2$ | 0.16 | 0.11 | 0.15 | 0.18 | 0.06 | 0.13 | 0.20 | 0.12 | 0.18 | 0.19 | 0.23 | 0.18 | 0.19 | 0.12 | 0.08 | 0.15 | 0.05 | 0.00 | 0.01 |
| $Cr_2O_3$ | 0.10 | 0.00 | 0.02 | 0.00 | 0.09 | 0.00 | 0.04 | 0.00 | 0.01 | 0.00 | 0.04 | 0.00 | 0.03 | 0.00 | 0.06 | 0.01 | 0.05 | 0.00 | 0.00 |
| MnO | 0.00 | 0.02 | 0.02 | 0.02 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.03 | 0.00 | 0.00 | 0.02 | 0.03 | 0.03 |
| $Fe_2O_3$ | 64.15 | 56.45 | 55.34 | 54.30 | 67.64 | 52.61 | 50.33 | 58.88 | 49.76 | 31.68 | 40.95 | 44.80 | 49.02 | 50.40 | 56.25 | 52.17 | 8.86 | 0.28 | 0.48 |
| NiO | 0.01 | 0.01 | 0.02 | 0.03 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.02 | 0.01 | 0.03 | 0.00 | 0.02 | 0.01 | 0.00 |
| $V_2O_3$ | 2.49 | 3.07 | 2.61 | 3.14 | 2.62 | 2.64 | 2.19 | 3.28 | 2.25 | 1.34 | 1.87 | 2.44 | 2.47 | 2.41 | 2.22 | 2.47 | 0.49 | 0.00 | 0.01 |
| Total | 87.76 | 78.34 | 79.37 | 76.12 | 89.28 | 76.55 | 79.58 | 84.55 | 74.26 | 85.41 | 84.19 | 78.69 | 81.96 | 75.45 | 77.39 | 80.59 | 4.67 | 96.61 | 98.05 |

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