Improved Regional Ties to Global Geochronology Using Pb-Isotope Signatures of Volcanic Glass Shards from Deep Water Gulf of Mexico Ash Beds

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ABSTRACT

Sedimentary beds rich in volcanic ash (ash beds) have been confirmed in several recent offshore Gulf of Mexico (GOM) exploratory wells. A petrographic/scanning electron microscope survey for volcanic glass shards on well cuttings and sidewall cores donated by the petroleum industry is currently ongoing at University of New Orleans (UNO). Fifteen separate ash beds have been documented in our preliminary survey. We have also determined the paleontological ages of these GOM ash beds with industry micro-paleo reports. The paleo-ages of these ash beds appear to be correlative with the ages of maximum flooding surfaces on industry sea-level curves.

Due to their distinctive log and seismic response, thick ash beds are ideal candidates for use as precise time markers in the GOM subsurface if they can be tied to known eruptive events. Based on proximity in time, we believe that the most likely sources for these ashes are the Huckleberry, Lava Creek, Mesa Falls, Bishop, and other eruptive events that occurred in the Yellowstone Plateau from 0.6 to 12 mya. These eruptions had enormous ash volumes that covered much of the ancestral Mississippi drainage area. Isotopic analyses of glass shards from GOM ash beds indicate a lead isotope signature that matches volcanic tuffs in the Yellowstone Plateau and precludes other ash sources for the GOM ash beds.

INTRODUCTION

Sedimentary beds rich in volcanic glass have been documented in 16 exploratory wells drilled in the Gulf of Mexico (GOM) on the Louisiana Outer Continental Slope (OCS). These occurrences are only a partial sample of the total distribution of ash deposited since the latest Miocene. Preliminary work on well-cuttings and sidewall cores donated to us from the petroleum industry indicates the presence of 15 separate ashes over a period ranging between 1 to 12 million years in age. This places these ash beds significantly younger than the volcanic activity from West Texas or the Sierra Madre of Mexico. Central American volcanic sources of this time period are known to have emitted airborne ash in the GOM, but these have been on the order of millimeters thick (Ledbetter, 1985), much too small to account for observed ash deposits up to 30 meters thick in the GOM. The remaining candidate for sourcing such large ash deposits is the western United States. There were a number of huge eruptions in this area over the last 12 million years, that would have directed ash-fall into the Mississippi River drainage basin (Figure 1). Thick ash beds of latest Miocene-Pleistocene age have been reported from the mid-continent (Izett and Wilcox, 1982), thousands of kilometers from their defined eruptive centers in the western United States. Volcanism in the western U.S. has been well documented, accurately dated, and in many cases has been both chemically and isotopically characterized. In most cases, ash from separate eruptions may be differentiated based upon these data.

All of the shards we have examined are silica-rich, and must have come from a rhyolitic volcanic source. This is not the composition of most of the Central American volcanic rocks over this time period. In searching for possible rhyolitic eruptions to source the observed GOM ash beds, we compiled a list of western United States eruptions complete with dates of eruption (see Table 1). We also approximated the dates of confirmed volcanic ash-bearing beds in the GOM by using the closest micropaleontologic marker (primarily foraminifera fossil assemblages) to date the bed. The ages of these ash beds, dated using micropaleontology, correlate satisfactorily with the absolute ages of western U.S. primary volcanic ash beds. We propose that the GOM ash beds are actually sourced by western United States volcanic activities of similar dates. Preliminary geochemical correlation using Pb-isotopic data confirm our idea and encourages continuing research to identify and describe the distribution of these ashes in deep water outer continental shelf (OCS) and other areas in the GOM subsurface.

ASH BEDS IN THE GULF OF MEXICO

GOM ash samples, retrieved from piston cores, have documented the presence of ash beds younger than 0.185 mya (Rabek et al., 1985; Thunell, 1976). A possible relation between Late Pleistocene climate, foraminifera biostratigraphy, and tephrochronology in the western GOM was reported (Kennett and Huddleston, 1972), but the ash occurrences were too few to make any definite connections. The ash beds encountered in these previous studies would not be identified in our study because the beds are too young, too shallow, and above surface casing. Volcanic glass detritus was identified as a major constituent in the Middle Frio fluvial formation of south Texas (Kerr and Grigsby, 1991) This Oligocene formation is much older than the section in which we have obtained samples from in the offshore GOM. In the Middle Miocene through Pleistocene subsurface section of the GOM targeted in this study, we know of one published study. In this study, a Pliocene ash of unknown source was fission-track dated and correlated for comparison to paleontological dates of proximal markers throughout a field area (Beard et al., 1976).

Several ash beds of Miocene to Pleistocene age have been reported in the mid-continent and Texas (Swineford, 1955; Izett and Wilcox, 1982). These ash deposits have been interpreted as primary ash falls many of which are several feet thick. We believe, however, that these are stream deposits of reworked ash similar to ash beds described by Sarna-Wojcicki et al. (1991). Many of the continental ash beds have been dated using mammalian paleontology
of encasing formations. Recently a number of the continental ashes have had absolute ages determined (Ward et al., 1993). Given the large estimated sizes of many of these eruptions, it is probable that volcanic ash introduced into the Mississippi River drainage area would have dominated clastic influx into the river systems immediately following eruption. The subsequent pulse of shard-rich clastics would have resulted in an ash-rich sediment to the shelf, where they were reworked and deposited as ash-rich turbidites in the deep water GOM. Redeposition of ash as turbidites has been reported by Huang (1980) in other locations worldwide.

**WESTERN UNITED STATES ERUPTIONS**

The numerous sites of ash bed exposed in the Mississippi River drainage area point towards volcanic sources on the North American continent for GOM ash beds that are, themselves, encased in materials transported in the ancestral equivalents of this drainage system. Most of the eruptions were concentrated in the Yellowstone area, the Snake River Plain, the Long Valley area of California and the Jemez Mountains area of New Mexico. These eruptions were very explosive, and some were extremely large. One eruption from the Yellowstone Plateau, the Huckleberry Ridge, is thought to have spewed 2500 km$^3$ of ash onto the western area of North America about 2 mya (Christiansen, 1991). It would actually be more surprising not to have found evidence of such an eruption in the GOM than to have found some. We have compiled a list of North American eruptive events from the literature (Table 1). All of these eruptions were silicic, contributing to their explosive nature, and could have produced ash of the composition which we have found in the GOM. Airborne ash deposits from Yellowstone eruptions have been documented as far away as Mississippi and onshore Louisiana (Christiansen, 1984).

The geochemical and isotopic compositions of these eruptions are well documented in the literature. Most can be discriminated from one another. It is possible, in most cases, to identify which eruptive center is responsible for producing a given ash bed,
<table>
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Table 1. Documented major western U.S. volcanic eruptions during the Pleistocene, Pliocene, and Middle to Late Miocene Epochs.

and to discriminate between separate eruptions from the same caldera. The chemical compositions and observed trends of the several large eruptions originating from Yellowstone permit identification of related ash beds. A good example of this is the use of lead isotopes to discriminate the Yellowstone ashes (Doe et al., 1992).

**AIMS**

The objective of this research is to test if ash-rich beds present in the latest Miocene to Pleistocene section in offshore Louisiana can be correlated to volcanic eruptions from the western United States over the same time period. We also test the validity of Pb-isotopic fingerprinting to confirm these correlations.

**METHODS**

Ash beds rich in volcanic glass shards can display distinctive sonic and density log responses. Ash beds can also produce “bright spots” on seismic profiles with high seismic amplitude, somewhat similar to hydrocarbon-bearing sandstones. Well logs were used to identify potential ash zones from which specific samples were examined for shards. In this manner, a number of sidewall core samples were retrieved from suspected ash beds. Drill cuttings were also available for ash zones that were below surface casing on wells without sidewall cores.

Volcaniclastic glass shards from samples were concentrated by use of a liquid of 2.5 specific gravity. This liquid caused the quartz, feldspar, and other heavy minerals to sink, and the lower density ash shards to float. These separations confirm the low-density nature of the shards, and the resulting density contrasts of ash rich beds with typical GOM clastic formations, as predicted by
their seismic and log characteristics.

The combination of several electric log curves was important in establishing the possible occurrence of ash-rich beds. The following general criteria were used.

1. Gamma-ray logs: Volcanic ash beds have high gamma-ray counts, similar to shales. In a few instances a spectral gamma-ray log was run, which separates the gamma into its component spectra due to uranium, thorium or potassium. The gamma-rays emitted from ash beds are primarily from thorium, while shales have particularly high potassium.


4. SP logs: Although not a direct indicator of ash, SP curves may be used to discount some non-ash lithologies, especially shale.

Based upon well log signatures, samples were obtained for many of the wells in which we suspected ash. Both well cuttings and a few sidewall cores were obtained from Shell Oil Company. Several Pleistocene ash beds that outcrop in the mid-continent (Izett and Wilcox, 1982) were also sampled for comparison to GOM ash samples.

The dates of the ash beds were determined using micropaleontologic methods, standard in the oil industry. Paleontologic reports were obtained for each well with a confirmed ash. The nearest paleo marker was used to determine the approximate age of the ash bed.

All of the samples were cleaned using an ultrasonic probe to disaggregate any clay coating on the surface of the glass shards. The slurry was passed through a 10-micron micro-sieve, also using ultrasonic energy. This process allowed the clays to be separated from the coarser mineral fraction. It also allowed the shards to be more easily recognized. An example of a shard before and after ultrasonic treatment is shown in Figure 2.

The coarser than 10 micron fractions were further separated by centrifuging in a high density liquid. Lithium Metatungstate (LMT) was used because the density is easily controlled by dilution with distilled water. The ash shards floated in an LMT solution with a specific gravity of 2.5 g/cc, which was dense enough to sink all of the quartz, feldspar, and other mineral components. The result is a very pure fraction of volcanic ash shards.

Grain mounts of the shards were prepared using Petrowooxy 7154. The shards were identified in thin-section by their distinct shard-like shape, as well as their amorphous behavior under crossed-nichols. The grain mounts were also carbon-coated for examination using the SEM. EDS spectra were collected for many shards to determine their overall chemical composition. Aliquots of the carbon-rich ash for several sample sites were analyzed for their lead isotope composition in the San Diego State University Stable Isotope Laboratory.

**Pb Isotope Analysis**

Pb isotopes were determined on the tuff fragments following methods similar to those described in Hanan and Schilling (1989). For the determination of Pb isotope composition, approximately 0.05 to 0.1 g of tuff fragments were acid washed in cold 2N HCl, followed by a wash in 1N HBr and finally a rinse in quartz-distilled H2O. The analyses were performed on a VG-SECTOR 54 mass spectrometer. Raw data were corrected for mass fractionation and machine bias based on replicate analyses of NBS SRM981 for Pb (using the values of Todt et al., 1984). The mass discrimination factor for Pb averaged 1.00127 ± 0.00004 (2σ) per mass unit. Total uncertainties in the Pb isotope ratios reported in Table 3 are <0.05% per amu, computed by error propagation of both sample and standard analyses. The Pb blanks were <100 pg for procedures, and are negligible.

**RESULTS**

Potential ash occurrences in rocks younger than 12 mya were identified by electric logs in more than 100 wells in offshore Louisiana (Fig. 3). To date, we have confirmed the presence of volcanic glass shards in 16 of these wells by separating the ash from well cuttings (Fig. 4). Examples of separated volcanic glass shards are displayed in Figure 5, along with the sections of the electric logs from where they were identified. The average thickness of ash beds was over ten meters. A few much thicker beds were also encountered. Many shards exhibit bubble casts, attesting to their explosive history. Shards from other beds were more pumice-rich. Most ash beds contain pristine glass shards, although variable degrees of alteration were noted. The shards are very silica-rich as evidenced by their EDS spectra, equivalent to a rhyolitic composition.

The stratigraphic positions of the confirmed ash occurrences, relative to industry paleo markers, are shown in Table 2.
DISCUSSION

Rhyolitic ash deposits, many meters thick, have been confirmed over a significant portion of the continental shelf in offshore Louisiana. These ashes are younger than 12 mya based upon their position relative to the nearest paleo marker. This places them significantly younger than the Oligocene - early Miocene volcanic activity in nearby Texas, and older than the high-silica eruptions of the latest Pleistocene, Mexican Neovolcanic belt (Mahood and Halliday, 1988). This raises the question of where these ashes were sourced. Based upon several lines of evidence, we propose that the GOM ash beds were sourced by western U.S. eruptions in the late Cenozoic.

We have documented ash beds more than 30 meters thick, although most are about ten meters thick. Beds over 30 meters thick are not likely to have been deposited as primary ash falls at such great distances to their source. It seems more likely that the beds were deposited as turbidites generated from reworked ash originally on the continent. A mechanism for the deposition of such thick ash deposits is from density flows across the continental shelf. The original source of the ash must have been on the continent. Yellowstone aged ash within turbidites off the California coast have been reported (Sarna-Wojcicki et al., 1987). Huang (1980) reports similarly redeposited ash in offshore Japan.

Ash beds of the appropriate age have been described on the continent, including Pleistocene ash beds in the mid-continent area. Several of these ashes have been accurately dated, both by paleo and absolute techniques. They have also been geochemically fin-

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Notes: Ages of paleo markers are from Styzen (1996). For time correlative purposes, we are gathering additional data on sizes and ages of eruptions which blanketed the Mississippi River drainage area during the Miocene. If successful, we will attempt to resolve more precise ages for the Miocene samples. *Sample #10 is ash confirmed by Beard et al., 1976.
Figure 3. Locations of wells with potential ash occurrences based on well log characteristics (not confirmed petrographically/SEM) in an assortment of GOM exploratory wells.

Printed to specific volcanic eruptions centered in the western United States. The mid-continent ashes are quite thick, and display ripple marks and other sedimentary structures suggesting fluvial deposition. Figure 6 illustrates an ash identified as reworked Huckleberry Ridge collected by the authors from Meade County, Kansas. This ash has a fission track age of 2.0 million years, coeval with the Huckleberry ridge eruption (Naezer, et al., 1973). Both mid-continent ash beds are thousands of kilometers from the eruptive centers. They must be reworked ash from air falls distributed over the fetch area of the stream system to which they belong. They are contained within the Mississippi drainage system (Figure 1) and are evidence of a source of reworked ash on its way to the GOM.

Volcanic activity to the south would be unlikely to cause such thick ash deposits on the Louisiana continental shelf. We do not know of a mechanism by which thin primary ash falls originally deposited in deep waters beyond the slope could be reworked up the slope and deposited as the thick ash beds found on the shelf. For the GOM ashes described in this report to be sourced from the Caribbean, Central America, or even Mexico, a significant amount of ash fall would be required to reach the Mississippi River Valley. This is a much greater distance than the proposed western U.S. source. It also ignores prevailing wind directions (Williams et al., 1990).

If the source of the GOM ash is on the continent, then there should be a relationship between the timing of western U.S. volcanism and the deposition of GOM ash. We have recognized a possible correlation, based upon micropaleontology, between the timing of western United States eruptions (Table 1) and the approximate dates of GOM ash beds (Table 2). The stratigraphic ages of Table 2 are consistent with eruptive events in Table 1 and suggests that a link between the North American volcanic eruptions and the volcanic ash beds in the GOM exists. In particular several ash beds close in time, to the Huckleberry eruptions have been confirmed. We have also found GOM ash beds that coincide with other Western U.S. eruptions. An offshore Louisiana ash bed with a fission track age of 3.1 ± 0.4 mya was reported by Beard et al. (1976) Although a source for the ash was not proposed, it is coincident with an ash fall noted in this study, suggesting sourcing by the Nomlaki eruption of California.

Volcanologists have established geochemical and isotopic fingerprints for specific eruptions based upon ash falls near the eruptive center. Particularly useful for discerning the western U.S. eruptions have been radiogenic lead isotopes. Preliminary Pb-isotopic data on ash from four GOM wells and two mid-continent occurrences illustrates the usefulness of this technique. Ash from wells near the Shell P1.78 paleo-marker plot within the Huckleberry Ridge field (Fig. 7), as does the Kansas sample. These Pb isotope signatures directly tie primary ash-falls at Yellowstone with reworked river deposits of the same age in the mid-continent and with turbidite deposits of similar stratigraphic
age in the GOM. The linking of these ash deposits represent one timeline across half of the North American continent at the Pliocene-Pleistocene boundary.

The other two ashes from the GOM, as well as the Texas outcrop sample, plot outside of the Huckleberry Ridge field, which supports their assignment to a different eruptive source. Sample GOM #13 and the Texas sample plot within the overall Yellowstone field, suggesting that it was sourced by a different Yellowstone eruption. We assign this ash to the Mesa Falls eruption, based upon its proximity to the Shell P1.58 paleo marker with an approximate age of 1.27 mya. GOM #13 also was assigned to paleo marker P1.58, but plots outside of the Yellowstone field using Pb-isotopes. Although it might have been sourced by another western U.S. eruption, there is insufficient isotope data to match its Pb signature. Future work will concentrate on establishing correlations to additional eruptions in the western U.S.

**CONCLUSION**

Several ash beds in the latest Miocene-Pleistocene are present on the Louisiana outer continental shelf in the Gulf of Mexico. We conclude that these ashes are reworked and re-sedimented from volcanic eruptions centered in the western United States.

Preliminary work, using lead isotopic signatures, establishes a correlation of ash in close proximity to the Shell P1.78 paleo marker to the Huckleberry Ridge eruption from Yellowstone at 2.0 million years ago. Considering the huge scale of the eruptions (up to 2500 km$^3$) and the large amount of reworked ash described across the mid-continent of the U.S., we propose that primary ash-falls overwhelmed the Mississippi River drainage system during an eruption. In essentially an instant in geologic time, this ash was transported ultimately to the GOM and deposited within turbidites. Each large eruption, therefore, has a subsequent ash bed of essentially the same age, and represents a timeline wherever it is found.

Ash beds are currently used in the GOM for correlation. Very little work is being conducted regarding their genesis and source. Continued investigation of ash in the GOM basin will build a database of ash deposits, with geochemical fingerprints that allow ash beds to be discerned from each other. We hope to establish several “time-lines,” useful in defining the sequence stratigraphy of the Gulf. The potential use of such a database in calibrating paleo markers and establishing a chronostratigraphy based upon ash occurrence will be of significance to the Louisiana oil industry. The possibility of each individual ash providing a “snapshot” of sediment pathways for a unique point in time is also significant.
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Figure 5. Well log strips over confirmed ash bearing beds and scanning electron microscope images of shards from sidewall cores.
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Figure 7. $^{208}_{\text{Pb}}/^{204}_{\text{Pb}}$ and $^{207}_{\text{Pb}}/^{206}_{\text{Pb}}$ versus $^{207}_{\text{Pb}}/^{206}_{\text{Pb}}$ covariation diagrams for four GOM wells and two midcontinent ash occurrences. All of the samples except GOM #13 fall within the isotope variation of the Yellowstone eruptions. Samples from GOM #9, GOM #16, and the Kansas outcrop plot within the Huckleberry Ridge A and B tuffs. GOM #13 and the Texas Outcrop sample plot near Mesa Falls/Lava Creek tuffs. Yellowstone fields are based on the Pb isotope data of Doe et al., (1982). Bandelier fields are from Pb isotope data of Ayuso and Smith (1994).


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