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Correspondence and requests for materials should be addressed to R. d. P. (e-mail: rolando.di-primio@hydro.com).

## Anomalous $^{17}\text{O}$ compositions in massive sulphate deposits on the Earth

Huiming Bao\*, Mark H. Thiemens\*, James Farquhar\*, Douglas A. Campbell\*, Charles Chi-Woo Lee\*, Klaus Heine† & David B. Loope‡

\* Department of Chemistry and Biochemistry, University of California San Diego, Mail Code 0356, La Jolla, California 92093, USA

† Institute of Geography, University of Regensburg, 93053 Regensburg, Germany

‡ Department of Geosciences, University of Nebraska Lincoln, Lincoln, Nebraska 68588-0340, USA

The variation of  $\delta^{18}\text{O}$  that results from nearly all physical, biological and chemical processes on the Earth is approximately twice as large as the variation of  $\delta^{17}\text{O}$ . This so-called ‘mass-dependent’ fractionation is well documented in terrestrial minerals<sup>1,2</sup>. Evidence for ‘mass-independent’ fractionation ( $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52\delta^{18}\text{O}$ ), where deviation from this tight relationship occurs, has so far been found only in meteoritic material and a few terrestrial atmospheric substances<sup>3</sup>. In the rock record it is thought that oxygen isotopes have followed a mass-dependent relationship for at least the past 3.7 billion years (ref. 4), and no exception to this has been encountered for terrestrial solids<sup>5</sup>. Here, however, we report oxygen-isotope values of two massive sulphate mineral deposits, which formed in surface environments on the Earth but show large isotopic anomalies ( $\Delta^{17}\text{O}$  up to 4.6‰). These massive sulphate deposits are gypcretes from the central Namib Desert and the sulphate-bearing Miocene volcanic ash-beds in North America. The source of this isotope anomaly might be related to sulphur oxidation reactions in the atmosphere and therefore enable tracing of such oxidation. These findings also support the possibility of a chemical origin of variable isotope anomalies on other planets, such as Mars<sup>6</sup>.

We have analysed sulphates from laboratory experiments and natural sources (Fig. 1). The  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  of seawater sulphate, evaporites, sulphate from microbial sulphate reduction experiments, and sulphates formed from mineral-sulphide oxidation in air or soils, all fall on the mass-dependent terrestrial fractionation line, given by the relationship  $\delta^{17}\text{O} = 0.52\delta^{18}\text{O}$ . The deviation from this relationship, defined as  $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52\delta^{18}\text{O}$ , is approximately zero ( $-0.04 \pm 0.05\text{‰}$ ,  $n = 36$ ). The central Namib Desert gypcretes and the Miocene volcanic ash-falls in the western United States, however, possess sulphate  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values that deviate from the terrestrial fractionation line. The sulphate  $\Delta^{17}\text{O}$  of Namib gypcretes ranges from 0.20‰ to 0.51‰ (Table 1), well outside the experimental error of  $\pm 0.05\text{‰}$ . Gypsum and other water-soluble sulphate minerals from Miocene volcanic ash deposits in Nebraska and South Dakota have strikingly large  $\Delta^{17}\text{O}$  values, up to 4.59‰, in contrast to the zero or slightly positive  $\Delta^{17}\text{O}$  found in adjacent

**Table 1 Isotopic compositions and occurrences of the Namib gypcretes**

Sample	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	Depth below surface (cm)
GOR13-2	12.4	6.8	0.34	5
GOR13-3	8.3	4.6	0.33	16
GOR13-5	10.5	5.9	0.42	36
GOR13-6	11.6	6.4	0.35	52
GOR14-6	12.2	6.6	0.29	40
GBB16-6	11.8	6.4	0.26	45
GBB17-5	9.8	5.3	0.20	16
GBB17-6	9.5	5.2	0.26	46
GBB17-8	11.3	6.1	0.26	66
AUS6-5	9.9	5.6	0.40	10
SWA6-1	12.6	7.0	0.40	1
SWA6-2	12.0	6.6	0.31	9 (crack)
SWA6-3	11.4	6.3	0.34	5
SWA6-4	13.2	7.3	0.40	24
SWA6-6	13.0	7.1	0.37	50
SWA6GYP	11.1	6.2	0.38	52
SWA6-7	10.1	5.8	0.51	70
SWA9-10	11.3	6.1	0.23	46

Samples from the same soil profile are grouped together. Soil profiles are listed with decreasing distance from the ocean. Isotopic compositions are given in SMOW.  $\delta^{18}\text{O} = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1,000\text{‰}$ , where  $R$  is the number ratio  $^{18}\text{O}/^{16}\text{O}$ .

soil and fluvial horizons (Table 2).

Sulphate minerals with  $\Delta^{17}\text{O} \approx 0\text{‰}$  are expected because thermodynamic and kinetic (including biological) processes such as evaporation, mineral-sulphide oxidation (by  $\text{Fe}^{3+}$  or air  $\text{O}_2$ ), and sulphate reduction generate mass-dependent compositions (Fig. 1). Therefore, sulphate minerals with positive  $\Delta^{17}\text{O}$  values, such as those found in the central Namib Desert gypcretes and the Miocene volcanic ash-falls in the western United States require a different process. The only documented terrestrial reservoirs with positive  $\Delta^{17}\text{O}$  are from the atmosphere. Oxidants such as  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  are known to have positive  $\Delta^{17}\text{O}$  values that range from 1 to more than 25‰ (refs 7–10). Others, like OH and  $\text{NO}_x$ , remain to be measured.

Tropospheric  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  in rainwater may transfer their positive  $\Delta^{17}\text{O}$  values to the product sulphate by *in situ* oxidation of surface minerals (for example, sulphides). Our measurement of the sulphate produced by marcasite ( $\text{FeS}_2$ ) oxidation in the air yielded  $\Delta^{17}\text{O} \approx 0\text{‰}$ , indicating that the *in situ* pathway is not the major source of positive  $\Delta^{17}\text{O}$ . A more likely source is the wet and dry atmospheric deposition of sulphate produced by atmospheric oxidation of reduced gaseous sulphur compounds. The anomaly can come from atmospheric oxidants such as  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$  or OH radicals as a result of aqueous or gas-phase S(IV) oxidation. A similar explanation was invoked to interpret positive  $\Delta^{17}\text{O}$  values (0.20‰ to 1.80‰) observed in aerosol and rainwater sulphate<sup>11,12</sup>. Although the mechanisms of these atmospheric processes are still subjects of intensive study, the connection between our  $\Delta^{17}\text{O}$ -positive sulphate minerals and atmospheric oxidation processes is unequivocal, as shown by the close association with a high flux of atmospheric reduced sulphur compounds in our two reported cases.

Gypcrete soils in the central Namib Desert occur extensively near the coast and gradually thin off and disappear at about 50–70 km from the coast, constituting one of the most extensive gypsum accumulations in Africa. On the basis of  $\delta^{34}\text{S}$ , meteorological, hydrological, and geological information, Eckardt and Spiro<sup>13</sup> suggest that sulphate in the Namib Desert originates mostly from biologically produced marine sulphur (that is, not derived from sea salt), particularly the oxidation of marine dimethyl sulphide (DMS). This conclusion is also supported by the lack of correlation between gypcrete accumulation and bedrock in this location and the positive correlation between gypcrete accumulation and the proximity to the ocean, a source of DMS. The Benguela Current,

**Table 2 Description of the Miocene volcanic ash-bed deposits**

Sample	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	$\delta^{34}\text{S}$	Description
Loope-1	12.5	11.1	4.59	0.67	Sand crystal from Scotts Bluff, Nebraska
Loope-2	12.1	10.6	4.36	0.98	As above; different crystal
BNP-27	10.9	8.5	2.84	1.72	Silt/sandstone in the Sharp Formation, Nortch Trail, BNP
BNP-SP-1	9.6	7.7	2.72	–	Rockyford Ash bed, Saddle Pass, BNP
BNP-SP-2	10.6	8.5	2.98	4.29	As above; different specimen
BNP-25-1	12.6	6.8	0.25	7.45	Channel deposits in the Sharps Formation, Nortch Trail, BNP
BNP-28	–0.9	–0.5	–0.02	–6.93	Clay/siltstone associated with vertebrate fossils in the Sharps Formation, Nortch Trail, BNP

Samples from Badlands National Park (BNP), South Dakota, are listed in stratigraphically descending order. Sulphate-oxygen and sulphur-isotopic compositions are given in SMOW and CDT, respectively.

which originated in the early Late Miocene (about 10 million years ago) off the west coast of South Africa and Namibia, provides upwelled waters extremely rich in phosphate, nitrate and silica, which support a rich population of phytoplankton<sup>14</sup> and a high DMS concentration in the local atmosphere. According to this interpretation, the anomalous  $\Delta^{17}\text{O}$  of the Namib gypcretes reflects chemistry associated with atmospheric oxidation of DMS.

Volcanic activity reached its maximum during the Oligocene in western North America<sup>15</sup>. Layers of volcanic-associated deposits are exposed throughout the Oligocene/Miocene continental deposits in

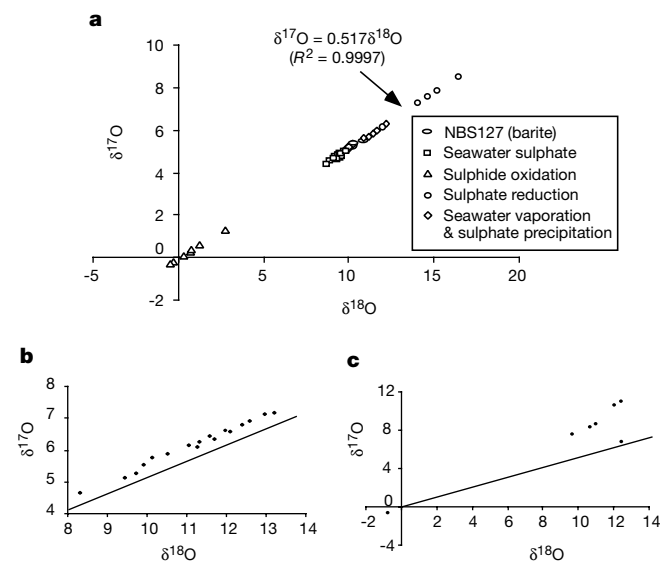
eastern Wyoming, South Dakota, North Dakota and Nebraska<sup>16,17</sup>. The current water-soluble sulphate content is about 0.02% in the Miocene Rockyford ash-bed (sample BNP-SP). It is well known that volcanic ash contains a significant amount of sulphate, occurring as sulphuric acid droplets that react to form gypsum or other sulphate minerals<sup>18</sup>. The occurrence of gypsum pseudomorph in the sandy Gering Formation may suggest high sulphate content in overlaid ash-beds. A volcanic origin for the sulphate sulphur is supported by its juvenile  $\delta^{34}\text{S}$  values (Table 2). The large sulphate  $\Delta^{17}\text{O}$  signatures from these widespread Miocene ash-beds indicate a link between the  $\delta^{17}\text{O}$ -anomaly and volcanic processes. Some of the sulphate  $\Delta^{17}\text{O}$  values are more positive than has been observed in sulphate aerosol, rainwater sulphate, and desert gypcrete. We expect the sulphate  $\Delta^{17}\text{O}$  value in volcanic ash will vary depending on distance from source and the nature of eruption.

Sulphate is one of a few non-labile oxygen-bearing ions (aquametal ions or oxo-anions)<sup>19</sup> that, once produced, are resistant to oxygen exchange with other ambient oxygen-bearing compounds (for example, water) under most surface environments. This chemical feature is essential for the preservation of the anomalous  $\Delta^{17}\text{O}$  signature in sulphate minerals.

The discovery of positive  $\Delta^{17}\text{O}$  values in minerals formed on Earth has important implications in Earth science. First, this is the first, to our knowledge, demonstration of a transfer of  $\delta^{17}\text{O}$  anomaly from atmosphere to crustal minerals. At this time, only a few approaches are available for probing ancient atmospheric conditions<sup>20–22</sup>. Sulphate  $\Delta^{17}\text{O}$  has the potential to be a tracer for ancient atmospheric ozone activity, chemistry in volcanic plumes, and the sulphur biogeochemical cycle in desert environments, where atmospheric sulphate is a major sulphur component. Second, it is interesting to evaluate recent findings of anomalous  $\Delta^{17}\text{O}$  for water, sulphate, and carbonate in SNC meteorites relative to coexisting igneous silicate minerals<sup>6,23,24</sup>. We document here a larger-magnitude  $\Delta^{17}\text{O}$  signature in terrestrial sulphate minerals than have been observed in SNC meteorites. Our observations are consistent with an atmospheric chemical origin for the SNC oxygen-isotope systematics. To establish the full implications of the  $\delta^{17}\text{O}$  anomalies found in terrestrial minerals, however, requires a fundamental understanding of the sulphur oxidation processes occurring in the atmosphere. The measurements of isotopic fractionation factors for the relevant oxidation reactions will permit quantification of the observations, as has been done for many other species<sup>3</sup>. □

**Methods**

Barite is precipitated from filtered and acidified solutions, which contain water-soluble sulphate from crushed gypcretes, sand crystals, volcanic ash-beds, and fluvial deposits. Molecular oxygen is extracted directly from barite following a newly developed method<sup>25</sup>, which employs a 30 W CO<sub>2</sub>-laser fluorination technique. Fine-grained barite was heated in a BrF<sub>3</sub> atmosphere, and more than 90% of the samples were analysed in duplicate. Samples are often loaded and analysed together with other  $\delta^{17}\text{O}$ -normal barites in one set. O<sub>2</sub> was run on a Finnigan MAT 251. We found no evidence for mass interference by NF<sub>3</sub> fragments or S compounds in our analyses. The samples with large positive  $\Delta^{17}\text{O}$  values were purified and reanalysed using a method<sup>26</sup> that quantitatively removes these compounds, after initial mass spectrometric analysis. No differences in  $\Delta^{17}\text{O}$  were observed. The results are highly reproducible and the difference between duplicate analyses is better than  $\pm 0.7\text{‰}$  and  $\pm 0.05\text{‰}$  for  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$ , respectively.



**Figure 1**  $\delta^{17}\text{O}$  versus  $\delta^{18}\text{O}$  for various sulphates. **a**, A fractionation line defined by major sulphate-involving processes on Earth. The seawater sulphate consists of sea water from La Jolla, California, and seawater sulphate adsorbed on the surface of amorphous and poorly crystalline ferric oxides from Red Seamount, Pacific Ocean. Sulphate from the oxidation of mineral-sulphides includes several non-evaporative gypsum minerals from glacial-till deposits in Akron, Ohio, and water-soluble sulphate from surface oxidation of marcasite (FeS<sub>2</sub>) exposed to air. The sulphate reduction experiment was conducted by adding organic-rich soil into a sealed tank of La Jolla sea water and allowing time for fractionation of oxygen isotopes by microbial sulphate reduction. Gypsum, other sulphate-bearing evaporitic minerals, and sulphate from final residual solution were collected from two seawater evaporation experiments conducted at 22 °C and 55 °C, respectively. **b**, Gypcrete and gypsum-bearing soils were collected from different soil horizons and different localities in the central Namib Desert. **c**, Volcanic ash and associated deposits were from the Miocene Arikaree Group, Nebraska and South Dakota (see Table 1 and Table 2 for details). The straight line in **b** and **c** is the terrestrial fractionation line ( $\delta^{17}\text{O} = 0.52\delta^{18}\text{O}$ ). The error bar (about  $\pm 0.7$  for  $\delta^{18}\text{O}$ ) was not plotted on the diagrams. Due to the high correlation between  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  during mass spectrometry analysis, the error for  $\Delta^{17}\text{O}$  is very small (less than  $\pm 0.05$ ). Thus, a thin rod with slope of 0.52 would best represent the actual point on the diagram. Delta values are given in SMOW.

Most samples give 28–33% O<sub>2</sub> yield during laser fluorination. We found by analysing NBS127 (NIST sulphate standard), seawater sulphate, and a low- $\delta^{18}\text{O}$  in-house standard that the raw  $\delta^{18}\text{O}$  values are consistently 9.4 lower than the reported ones, owing to the incomplete O<sub>2</sub> generation. The correction factor is also verified by more than a dozen natural sulphate samples—that have been analysed using both the laser-fluorination method and the graphite reduction/CO<sub>2</sub>-fluorination method<sup>27</sup>—that normally reach a 85% to 100% O<sub>2</sub> yield in our laboratory. This comparison also verifies that the incomplete O<sub>2</sub>-generation using a CO<sub>2</sub>-laser does not deviate from the slope of 0.52. Thus, the reported  $\delta^{17}\text{O}$  value is increased by 4.89‰.  $\delta^{34}\text{S}$  was analysed using the SF<sub>6</sub> method<sup>28</sup>. In this report, all  $\Delta^{17}\text{O}$  values are calculated on the basis of raw  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values. We use the linear equation to calculate  $\Delta^{17}\text{O}$  because all the raw  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values are close to the vicinity of the origin and the range of  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values among different samples are small.

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Correspondence and requests for materials should be addressed to H. B. (e-mail: hbao@chem.ucsd.edu).

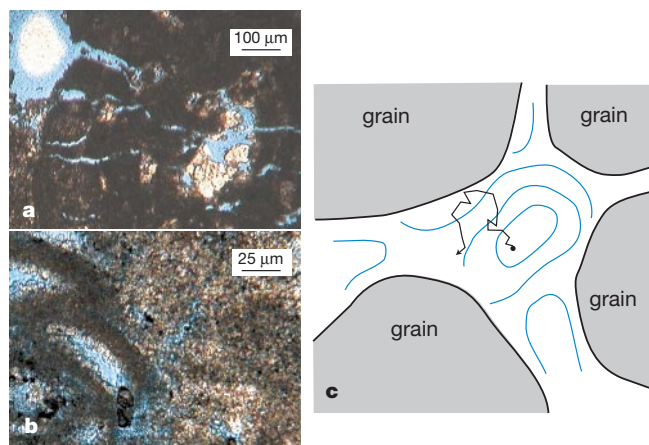
## Determining multiple length scales in rocks

Yi-Qiao Song, Seungoh Ryu & Pabitra N. Sen

Schlumberger-Doll Research, Old Quarry Road, Ridgefield, Connecticut 06877, USA

Carbonate reservoirs in the Middle East are believed to contain about half of the world's oil<sup>1</sup>. The processes of sedimentation and diagenesis produce in carbonate rocks microporous grains and a wide range of pore sizes, resulting in a complex spatial distribution of pores and pore connectivity<sup>2</sup>. This heterogeneity makes it difficult to determine by conventional techniques the characteristic pore-length scales, which control fluid transport properties. Here we present a bulk-measurement technique that is non-destructive and capable of extracting multiple length scales from carbonate rocks. The technique uses nuclear magnetic resonance to exploit the spatially varying magnetic field inside the pore space itself—a 'fingerprint' of the pore structure. We found three primary length scales (1–100  $\mu\text{m}$ ) in the Middle-East carbonate rocks and determined that the pores are well connected and spatially mixed. Such information is critical for reliably estimating the amount of capillary-bound water in the rock, which is important for efficient oil production. This method might also be used to complement other techniques<sup>3–5</sup> for the study of shaly sand reservoirs and compartmentalization in cells and tissues.

Nuclear magnetic resonance (NMR) is often used to investigate porous media by applying external magnetic field gradients in a fashion analogous to X-ray diffraction in determining the size of cells<sup>6</sup> and pores<sup>7–9</sup>. In fact, when a sample is placed in a uniform magnetic field, a spatially varying field and its gradients appear naturally inside the pore space as a result of the magnetic susceptibility contrast between the host solid material and the pore-filling fluid<sup>10</sup>. This field is called the internal field,  $B^i$ , and it can be large enough in natural materials such as rocks<sup>11–14</sup> to interfere with the



**Figure 1** Thin-section micrographs of the pore space in Thamama carbonate rocks and an illustration of the internal magnetic field. **a, b**, The blue regions are pores filled with blue epoxy before sectioning. Pores of size a few  $\mu\text{m}$  to about 100  $\mu\text{m}$  are clearly visible. The smaller pores show up as different level of shades owing to limited resolution. It is crucial to determine these length scales in understanding the transport properties. **c**, Diagram of the typical pore space, internal magnetic field  $B^i$  and diffusion. The blue lines illustrate the constant  $B^i$  contours (the component along the external field) reflecting the local pore geometry. The magnetization decay due to diffusion in  $B^i$  is used to characterize the pore sizes.