

Chlorine stable isotopes in sedimentary systems: does size matter?

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ABSTRACT: Stable isotope abundances vary because of size (atomic mass) differences. The chlorine stable isotope system was one of the first described theoretically, but had a slow, disappointment-strewn development, relative to other elements. Method improvement gave only small, but significant, differences ($\sim 1\text{‰}$) in compositions of geological materials. Eventually, brines and groundwater chlorides gave larger differences ($\sim 5\text{‰}$). Physical processes like diffusion and adsorption, probably are the main controls of groundwater compositions. In contrast, the processes producing brine compositions are still enigmatic and need further work for full understanding. Recent work on anthropogenic groundwater contaminants (chlorinated aliphatic hydrocarbons and perchlorate) shows variations resulting from manufacturing processes; implying possibilities of tracing sources. However, they are subject to microbial degradation, producing much larger fractionations ($\leq 15\text{‰}$), but therefore offering better possibility of monitoring natural attenuation. So atomic size is important to give isotopic fractionation and the size of fractionation matters, allowing observation of otherwise undetectable processes.

1 INTRODUCTION

This paper aims to give a short and selective history of the frustrating development of chlorine stable isotope geochemistry. Readers may be depressed by the apparently small return of science from the immense investment of effort expended by the pioneers in this area, but please do read on because there really is a happy ending.

I include a brief description of the technology of analysis, which has been and still is one of the key factors both allowing and restraining progress. Some examples of its application will indicate the scope of the method to produce large and characteristic isotopic fractionation values. Because of its relatively low chemical reactivity in sedimentary systems, chlorine demonstrates fewer effects of normal isotopic fractionation but therefore has the power to record physical processes.

2 HISTORY

2.1 *Early history*

In the late 1850s Cannizzaro resurrected the idea, put forward by Avogadro 50 years before, that equal volumes of gas contained equal numbers of molecules. This allowed him to refine estimates of mo-

lecular and atomic weights by weighing the gases and relating them to the weight of hydrogen. All atomic weights were integer multiples the weight of hydrogen, with the exception of chlorine, 35.5. It was not until Aston developed what was the effectively the mass spectrograph, a modification of Thompson's Positive Ray apparatus, that the non-integer atomic weight was confirmed to be the result of the abundances of two isotopes, ^{35}Cl $\sim 75\%$ and ^{37}Cl $\sim 25\%$ (Aston, 1919).

2.2 *Later history*

In a classic theory paper, Urey (1947) calculated the result of the equilibrium isotopic fractionation between perchlorate and hydrogen chloride molecules to be a massive isotopic difference in $^{37}\text{Cl}/^{35}\text{Cl}$ of 9.2% (more usually expressed now in parts per thousand as 92‰). This should have been measurable by the instruments of the day but was not found. In fact the major advance in analytical capability came from the various developments from two laboratories, those of Nier and McKinney in the period 1946 to 1955. That work produced the double collector mass-spectrometer, allowing stable isotope measurements to be made routinely to a precision of better than 1‰ (Nier, 1947; McKinney et al., 1950). However no one was able to measure any significant natural variations in chlorine stable isotope abundance ratios. Hoering & Parker (1961) analyzed 81

samples, including natural perchlorate and chloride from Chile, again with no detectable variation.

Further development of the method by the research group in the University of Arizona, finally improved the analytical precision to about 0.25‰ (Kaufmann (1984; Kaufmann et al., 1984). This gave hope that chlorine stable isotope geochemistry might start to follow the examples of the other light stable isotope systems, like carbon or sulfur, and show significant variations in ocean waters of different geological ages as well as characterizing geochemical processes. In the next ten years, although the Arizona group measured the first natural variations to be observed, the range of Cl isotope ratios in more than 200 samples of all geological ages was disappointingly small. Most samples were near to the value for modern seawater, adopted as the reference standard. The total range extended from 1.5‰ less than seawater chloride to just over 2‰ more.

Subtle further refinements of the technique by Eggenkamp (1994) now allow an analytical precision of about 0.05‰. Despite the increased data quality, analysis of more than 200 other geological samples by 1994 had produced a range from 2.5‰ less than seawater chloride to just over 1.5‰ more.

3 MEASUREMENT TECHNIQUES

The methods referred to above all measure the sample in the form of a gas. However Xiao and Zhang (1992) pioneered use of a technique, Thermal Ionization Mass Spectrometry (TIMS), previously used for measurement of radiogenic isotope ratios. Both of these commonly used methods for measurement of chlorine isotope ratios require that the sample to be converted into an appropriate chemical form from which it is ionized so that the different masses may be separated in a magnetic sector mass spectrometer. Results are reported as the difference of the $^{37}\text{Cl}/^{35}\text{Cl}$ ratio in the sample from that ratio in a standard reference material, $\delta^{37}\text{Cl}$, in parts per thousand, ‰.

$$\delta^{37}\text{Cl} = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} * 1000 \quad (1)$$

where $R = ^{37}\text{Cl}/^{35}\text{Cl}$.

Positive, negative and zero δ values indicate respectively, greater, less and the same relative abundance of the trace isotope compared with the standard.

This formulation, evolved from one of the methods by which isotope measurements are made but is used for both. In fact, there is no single standard curated and distributed by a single agency, as is the case for hydrogen and oxygen. However, Kaufmann et al. (1984) showed that all ocean water chloride had the same isotopic composition within the limits of measurement precision and defined the standard as SMOC, Standard Mean Ocean Chloride, analo-

gous with SMOW, Standard Mean Ocean Water, the standard for H and O.

3.1 Sample preparation agonies

For both types of measurement chlorine has to be in a specific, chemically pure form, methyl chloride for dual inlet stable isotope ratio mass spectrometry (SIRMS) and cesium chloride for thermal ionization mass spectrometry (TIMS). Without going into details, both approaches require analyst time, skill and patience.

There are frustrations associated with both techniques. In the case of analysis of chlorinated aliphatic hydrocarbons, commonly analyzed materials, organic chloride has to be separated as inorganic chloride ion and then converted into CsCl for TIMS analysis. The situation is even worse for SIRMS, where the organic Cl is separated by conversion to an inorganic chloride, precipitated as insoluble AgCl which is then converted back to organic methyl chloride. The main features of each of the isotopic analytical techniques are described very briefly below.

3.2 Comparison of SIRMS and TIMS

For SIRMS the sample is in gaseous form, methyl chloride. After introduction to the mass spectrometer, is ionized by electron bombardment. Introduction of the sample gas is alternated repeatedly with reference gas of known isotopic composition. This allows multiple direct estimates to be made of their difference in isotope ratio in about 15 minutes. Minimum sample size is ≤ 4 micromole. Reproducibility of analysis for the whole analytical procedure is $\leq 0.10\%$ (2σ).

In TIMS the CsCl solution, prepared from the sample Cl, is evaporated on a filament to form a solid that is ionized by resistive heating of the filament in the mass spectrometer. Multiple readings of the sample isotope ratio are taken over a period of hours. Standards can be run as samples to confirm the calibration of the mass spectrometer. Precision for a single run is $\leq 0.2\%$ but to determine the value relative to a standard, which also has the same uncertainty, the overall uncertainty is about 0.3‰ (2σ). To compensate for this, sample size can be as little as 0.3 micromole or less.

Godon et al. (2004) showed that a large variety of different seawater samples all gave the same result within error, thus confirming the use of SMOC as a standard. They also showed that both methods give comparable mean values for samples near to that of the standard but that more extreme values may not. However, part of the discrepancy may be due to the fact that in TIMS analysis the result may be changed by the amount of sample loaded onto the filament.

To summarize the points made above, whichever method is used, a lot of effort and time is needed to make any measurements and those made on sedi-

mentary materials showed very little variation in comparison to the larger ones of other stable isotope systems.

4 ISOTOPIC FRACTIONATION PROCESSES

4.1 Crystallization

Eggenkamp (1994) performed careful experiments crystallizing sodium, potassium and magnesium chlorides from aqueous solutions, but only NaCl gave a fractionation factor significantly larger than the uncertainty. The solid had a value $+0.24\text{‰}$ ($0.07\ 1\sigma$). The implication of this result is that during continued evaporation of seawater, the first-formed halite will have a positive value relative to SMOC. The residual seawater will have lost more ^{37}Cl relative to ^{35}Cl to the precipitate and consequently will be relatively depleted in the former, giving it a slightly negative $\delta^{37}\text{Cl}$ value. Continued evaporation will produce more negative values for the residual brine and a succession of precipitates which will track those values, but 0.24‰ more positive. Thus, evaporite salts may even have negative SMOC values. The systematic shift of isotope values dependent on the extent of completion of a reaction can be modeled as a Rayleigh Fractionation process. Eggenkamp (1994) used this result to interpret data on halite and other evaporite minerals from cores of Late Permian Zechstein salts. Successive analyses traversing vertically upwards in a core showed repeated sequences of more negative $\delta^{37}\text{Cl}$, which then reverted to a more positive value in a relatively short vertical distance. Each sequence represents evaporation of a batch of marine brine terminated by recharge from a volume of new seawater. The sequences correspond to Zechstein evaporite cycles defined by the changes in mineral composition.

4.2 Diffusion

Variations of chloride concentration in pore-waters correlated with $\delta^{37}\text{Cl}$ could be interpreted as preferential diffusion of ^{35}Cl relative to ^{37}Cl (Desaulniers et al., 1986; Eggenkamp et al., 1994). Although the effects were quite small and the uncertainties relatively large, the trends were persuasive, if not quantitative. The theory of diffusion is well established but predicting isotopic diffusion coefficients also requires knowledge of the chloride ion's physical properties and especially its interaction with its local water molecules. Consequently, Coleman et al. (2001) had to resort to laboratory experiments to determine the ratios of chlorine isotope diffusion coefficients under various conditions of temperature and chloride concentration. There are two points of significance in the results (e.g. Fig. 1). They show large and consistent relative depletion of ^{37}Cl of up to approximately 2‰ in the diffusion front; and a

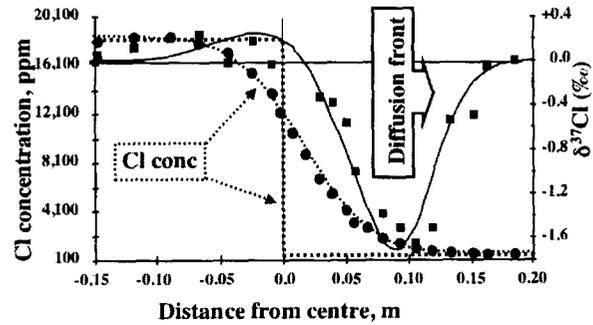


Figure 1. Laboratory experiments to measure the differential diffusion of ^{35}Cl and ^{37}Cl to produce a large change in $\delta^{37}\text{Cl}$.

corresponding, small relative enrichment in ^{37}Cl in the residual brine, from which ^{35}Cl has diffused faster. These data were used to estimate times of large-scale diffusion in natural systems (Section 7).

4.3 Microbial processes

There has been some effort to measure isotopic fractionation associated with microbial degradation of chlorinated hydrocarbon solvents and of perchlorate. This is because of their significance as environmental pollutants. In both cases, for either natural or engineered bioremediation, the $\delta^{37}\text{Cl}$ values of the residual contaminant and of the reaction product can indicate the extent of completion of the process. If the fractionation factor is constant, the reaction progress may be modeled as a Rayleigh fractionation process. This is best exemplified by the data for microbial perchlorate reduction shown in Figure 2 (Coleman et al., 2003). In this case reduction of perchlorate produces chloride approximately 15‰ more negative than the starting material. The residual perchlorate shows an increase in $\delta^{37}\text{Cl}$ as a precise function of the extent of completion of the reduction. Equally, the accumulated chloride independently can give the same information. Together, the chloride and perchlorate data at any stage, can be checked for chlorine mass and isotopic balance to validate the interpretation. The dramatically large isotopic fractionation factor allows the data for such processes to be interpreted even if there is presence of background values of natural chloride.

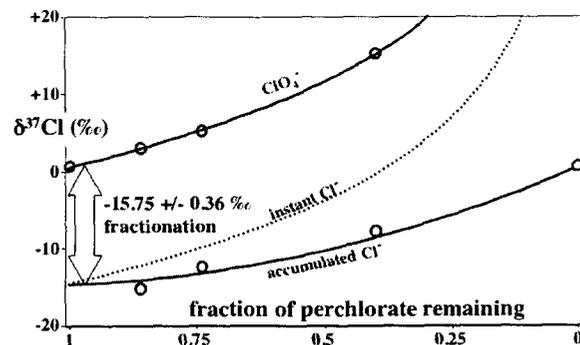


Figure 2. Microbial reduction of perchlorate to chloride, showing Rayleigh fractionation behavior.

Microbial dechlorination of chlorinated aliphatic hydrocarbon (CAH) solvents like tetrachloroethene (perchloroethene or PCE) is more complex since it may proceed in stages not necessarily mediated by the same type of microbe. Each stage may remove just one or maybe two chlorine atoms from the molecule as dissolved chloride producing successively trichloroethene (TCE), dichloroethene (DCE) and vinyl chloride. The results of Numata et al. (2002) showed a large range of isotopic fractionation values for dechlorination of TCE to cis-DCE and PCE to cis-DCE. However, their method did not permit separation of different chlorine-bearing molecules and rigorous checking by mass balance calculations. Their results gave consistent fractionation factors with chloride from TCE 5‰ to 6‰ more negative than the original material. Their results for dechlorination of PCE were very variable.

5 OIL-FIELD BRINES

5.1 Waters in clastic oil-field reservoirs

The first really sizeable chlorine isotope variations observed consistently were values ranging from near zero to -4.2‰ in samples of oil field brines from the Forties Field, reported at the WRI-7 meeting (Coleman, 1992). Despite the time since then, there is still no clear understanding of how these values are generated. Similar, negative values down to -5‰ occur in waters from Oseberg Field too (Ziegler et al., 2001). These data give information on routes and processes of mixing of distinct fluids.

Despite the technical difficulty of making chlorine isotope measurements, Eggenkamp and Coleman (2000) resurrected a chemical procedure published in 1895 that allowed separation of bromine from chlorine and made $\delta^{81}\text{Br}$ measurements on the Oseberg samples. The results are shown in Figure 3. So we are now in the situation where we can explain neither the chlorine nor bromine isotope compositions of these waters and their negative correlation implies at least a mixture of two components where different processes control the isotopic fractionations of the two elements.

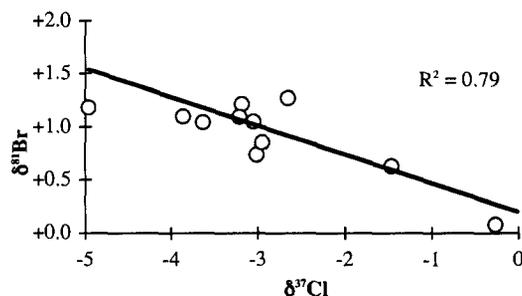


Figure 3. Negative correlation of chlorine and bromine stable isotope compositions from Oseberg oil field waters.

5.2 Water in carbonate oil-field reservoirs

A recent study of a large carbonate reservoir aimed to address not only the problem of showing admixture of different fluids, but also aimed to use the intrinsic information in the data to identify whether the water came from fracture or matrix permeability. The work involved not only measurements of field samples but also laboratory simulations of compaction and stress-induced fracture permeability. The other self-imposed difficulty was to use only the trace water extracted from produced oil. Despite the complexity of the data set, Poszwa et al. (2003) produced the results shown in Figure 4.

The effects are small in the experiments but relate qualitatively to the expected direction of fractionation, where processes like diffusion and adsorption will slightly enhance the relative abundance of ^{35}Cl in the micro-permeability of the matrix. The field data fortunately showed a much larger range of $\delta^{37}\text{Cl}$ values (-0.9 to -1.4‰), that were independent of brine chemical compositions but related to the permeability in the same way expected from the laboratory simulation experiments.

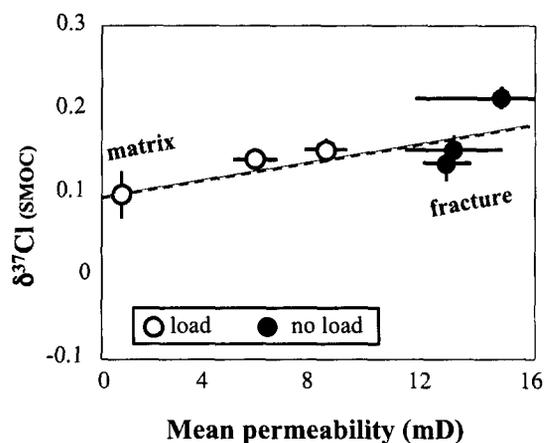


Figure 4. Relationship of $\delta^{37}\text{Cl}$ and permeability of chalk cores subjected to controlled imposed stress.

6 CONTAMINATED LAND

6.1 Contaminated land – Chloride pollution

There are number of cases in the UK where there is a plume of chloride in groundwater down-flow from a land-fill site, despite carefully engineering a very low permeability liner to retain the waste and its aqueous leachate. Analysis of leachate, nearby and control groundwaters produced a wide range of values for Cl concentrations and isotopic compositions (Loomis et al., 1998). It is clear from Fig. 5 that the high values of chloride in the plume are not the result of admixture leachate with groundwaters.

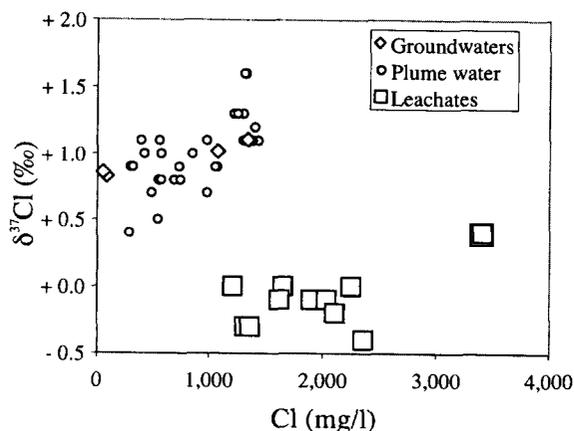


Figure 5. Chloride concentrations and isotopic compositions from a land-fill site and nearby locations

In this case there is a rational explanation for the results. The landfill site is a former quarry where clay was extracted for brick making. The clay is organic rich and also contains minor amounts of sulfide. The process of clay extraction exposed the sulfide to aerobic oxidation, which resulted in a local low pH environment allowing leaching of chloride from the clay.

6.2 Contaminated land – CAH

The microbial dechlorination fractionation process described in Section 4.3 indicated that successive chlorine atoms were stripped from the CAH. An attempted application of this approach to a field site resulted in a small but useful data set (Fig. 6).

There were two surprises from these data: they appear to show a relationship between carbon and chlorine isotope values and the isotope data relate to the concentrations. Although unexpected in terms of the microbial process, it seems that there is complete rather than step-wise dechlorination occurring indicated by the increase in carbon isotope values as the process progresses. Although, the fractionation factor has not been calibrated in the laboratory the results are consistent with a Rayleigh fractionation process and extrapolation back may constrain the original composition of the TCE.

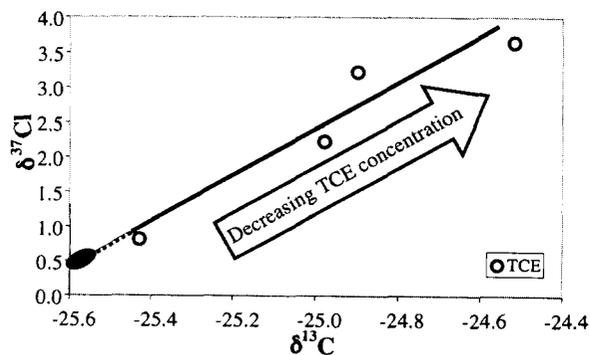


Figure 6. Carbon and chlorine isotopic values of TCE from a contaminant plume. The solid ellipse at the bottom left of the line indicates a possible, original value for the TCE.

7 RADIOACTIVE WASTE SITES

Two case studies are considered that show the value of the chlorine isotopes in obtaining both positive and negative information about the potential suitability of a site for construction of an underground test laboratory to investigate radioactive waste storage problems. The deliberately indirect phrasing in the previous sentence indicates the degree of public sensitivity to such issues and not only geoscientific criteria are important in such decisions. The two case studies were part of a larger program of research of the French organization ANDRA. The aim in both cases was to define the hydrodynamic stability of the sub-surface waters, since a site where there had been little flow in the past offered the promise for future lack of disturbance too.

7.1 Vienne Site, France

The rocks are fractured granite with pore-waters that show a concentration profile implying a possible diffusive gradient (Fig. 7). However, $\delta^{37}\text{Cl}$ data indicate that there has been no detectable diffusion.

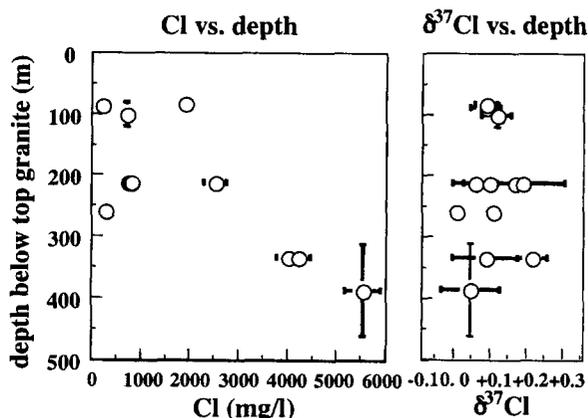


Figure 7. Variation of chloride with depth at the Vienne Site, but without corresponding variation of $\delta^{37}\text{Cl}$ values.

The reason for this definitive negative conclusion is obvious by reference to Figure 1. As well as the negative $\delta^{37}\text{Cl}$ at the diffusion front, caused by faster migration of the ^{35}Cl , there is a complementary increase in $\delta^{37}\text{Cl}$ in the residual source material. It is clear that this is not the case here and there is no evidence of diffusion in the Vienne Site and more energetic advective mixing is operating.

7.2 Gard Site, France

In contrast to the Vienne Site, the Gard Site is a marine sedimentary sequence of very low permeability fine-grained calcareous mud-rocks. Above and below the 400-meter thick mudrock succession there are highly permeable marine sands. During the Oligocene the system suffered tectonic activity and a lateral extension of the system was folded allowing erosion of a fold limb and ingress of meteoric water to the permeable sandstones. This activity replaced

the marine pore-fluids above and below the mudrocks with freshwater and thus establishing two salinity gradients. Unlike the Vienne Site, in this case it appears that diffusion has really occurred (Coleman et al., 2001). The salinity profile and the associated $\delta^{37}\text{Cl}$ data are shown in Figure 8.

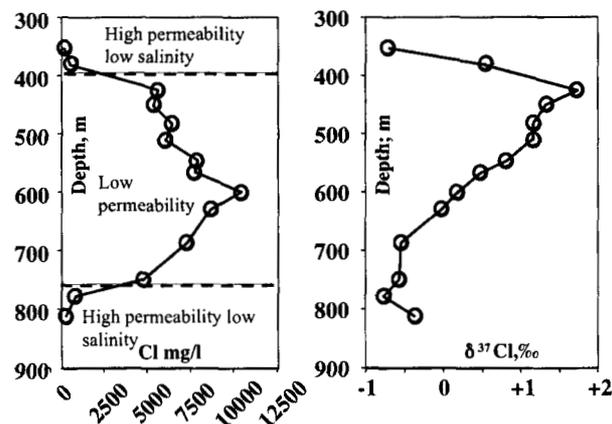


Figure 8. Chlorine and $\delta^{37}\text{Cl}$ variation with depth at the Gard Site, showing evidence of large-scale natural diffusion.

The salinity profile shows clearly a double diffusion system, with the assumed original seawater pore-fluid in the mudrock. If its original salinity was similar to the modern value of just over 20,000 mg/l there has been considerable loss even from the center of the formation. This is supported by the isotopic evidence, which again on the assumption that the marine pore-fluid had an isotopic composition like modern seawater, was originally 0‰. The more positive values in the center and negative ones at the two diffusion fronts are strong evidence of diffusion. However, the lack of vertical coincidence of the salinity and $\delta^{37}\text{Cl}$ maxima, implies occurrence of another process, probably related to mudrock compaction prior to diffusion. Using a normal Fick's law diffusion model and the diffusion coefficients mentioned in Section 4.2, it is possible to compute a diffusion time of 15.5 million years, indicating a remarkably stable hydrodynamic system. It is also gratifying to see the extrapolation of a two-week diffusion experiment over a length scale of 40cm extrapolated to 15 million years and 400 meters.

8 CONCLUSIONS

From the above case studies it is apparent that size does matter, not only in causing isotopic fractionation but also in producing effects sufficiently large to be significantly above measurement uncertainties. However, in most of the examples above it is also clear that size is not enough and what one does with the data is equally important. In particular there are now a number of very large and reproducible effects for which there is either no or insufficient explanation in terms of basic understanding of relevant

processes. However, as in the earlier days of this branch of science, it will be easier to make advances in understanding, if the means of making high precision measurements becomes faster and easier.

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