

ISOTOPIC MASS FRACTIONATION LAWS AND THE INITIAL SOLAR SYSTEM $^{26}\text{Al}/^{27}\text{Al}$ RATIO. A. M. Davis^{1,2,3,4}, F. M. Richter^{2,3,4}, R. A. Mendybaev^{1,3}, P. E. Janney^{1,4}, M. Wadhwa^{1,4}, K. D. McKeegan⁵, ¹Chicago Center for Cosmochemistry, ²Enrico Fermi Institute, ³Department of the Geophysical Sciences, The University of Chicago, Chicago, IL 60637 (a-davis@uchicago.edu), ⁴Isotope Geochemistry Laboratory, The Field Museum, Chicago, IL 60605. ⁵Department of Earth and Space Sciences, University of California, Los Angeles, CA 90024.

Introduction. Excess ^{26}Mg from the decay of ^{26}Al was discovered in 1976 by thermal ionization mass spectrometry of mineral separates from a CAI [1]. Since that time, the ^{26}Al - ^{26}Mg system has been of great interest because of its potential for precise early solar system chronology. Until recently, most of the data generated was by ion microprobe using a single collector and data that most precisely defined the early solar system $^{26}\text{Al}/^{27}\text{Al}$ ratio was based on ion probe analyses of minerals with high Al/Mg ratios. In the last few years, multi-collector ICP and multicollector ion probe mass spectrometry have made possible high precision magnesium isotopic analyses that provide chronologically useful data on low-Al/Mg phases. Some of these studies have suggested that the initial solar system $^{26}\text{Al}/^{27}\text{Al}$ ratio may have been higher than the “canonical” value of 4.5×10^{-5} [2,3].

Magnesium has three isotopes, 24, 25 and 26, and isotope ratios vary in solar system objects by mass dependent fractionation and by the effects of ^{26}Al decay. In order to infer the effects of the latter, the exact behavior of mass dependent fractionation must be known. CAIs, where most ^{26}Al - ^{26}Mg studies are done, typically have mass fractionation effects of a few ‰/amu and so-called FUN inclusions have larger mass fractionation signatures. The algorithm or “law” used to correct CAI data for natural mass fractionation effects can significantly affect the inferred amount of radiogenic ^{26}Mg , especially in cases where the degree of mass fractionation is large and/or the Al/Mg in the phase analyzed is small. A variety of fractionation laws have been used to correct isotopic data. We review these laws, describe the results of experiments in which the mass fractionation law has been determined for vacuum evaporation of CAI compositions and recalculate a number of published supercanonical $^{26}\text{Al}/^{27}\text{Al}$ ratios.

Mass fractionation laws. In their review of ^{26}Al - ^{26}Mg data, MacPherson et al. [4] discussed fractionation laws and suggested that since Rayleigh fractionation of Mg atoms described fractionations in FUN inclusions fairly well, this law should be used to correct CAI data. They plotted deviations of various laws relative to the Rayleigh law, and we will follow that practice here. For this discussion, it is convenient to express magnesium isotope ratios in two ways: the familiar delta notation,

$$\delta^{25}\text{Mg} = \left[\frac{\left(^{25}\text{Mg}/^{24}\text{Mg} \right)_{\text{samp}}}{\left(^{25}\text{Mg}/^{24}\text{Mg} \right)_{\text{std}}} - 1 \right] \times 1000, \text{ similarly for } \delta^{26}\text{Mg},$$

and

$$\phi^{25}\text{Mg} = 1000 \times \ln \left[\frac{\left(^{25}\text{Mg}/^{24}\text{Mg} \right)_{\text{samp}}}{\left(^{25}\text{Mg}/^{24}\text{Mg} \right)_{\text{std}}} \right], \text{ similarly for } \phi^{26}\text{Mg}.$$

Mass fractionation laws can be divided into two broad categories: those that are linear on plots of $\delta^{25}\text{Mg}$ vs. $\delta^{26}\text{Mg}$ and exponential processes that are linear on plots of $\phi^{25}\text{Mg}$ vs. $\phi^{26}\text{Mg}$.

The simplest law used for correction of mass fractionation data is the “linear” law [4]:

$$\Delta^{26}\text{Mg}^* = \delta^{26}\text{Mg} - \delta^{25}\text{Mg}/0.5, \quad 1$$

where $\Delta^{26}\text{Mg}^*$ indicates radiogenic ^{26}Mg . This law was commonly used for ion microprobe data on high Al/Mg phases. For typical precision of 1–2 ‰, this law was effective at high Al/Mg, but gives significant errors at low Al/Mg. A closely related law,

$$\Delta^{26}\text{Mg}^* = \delta^{26}\text{Mg} - \delta^{25}\text{Mg}/0.5189, \quad 2$$

was used because it describes the slope of terrestrial samples plotted on a $\delta^{25}\text{Mg}$ vs. $\delta^{26}\text{Mg}$ plot [2].

The most commonly used law for TIMS analyses is the “exponential” law [5]. Here,

$$\frac{\left(^{25}\text{Mg}/^{24}\text{Mg} \right)_{\text{samp}}}{\left(^{25}\text{Mg}/^{24}\text{Mg} \right)_{\text{std}}} = \left(\frac{24.985837}{23.9850419} \right)^{\xi} \quad 3$$

and

$$\Delta^{26}\text{Mg}^* = \left[\frac{\left(^{26}\text{Mg}/^{24}\text{Mg} \right)_{\text{samp}} \times \left(\frac{26.982593}{23.9850419} \right)^{-\xi}}{\left(^{26}\text{Mg}/^{24}\text{Mg} \right)_{\text{std}}} - 1 \right] \times 1000, \quad 4$$

where the constants are the exact masses of the magnesium isotopes. This law gives a slope of 0.5110 on a plot of $\phi^{25}\text{Mg}$ vs. $\phi^{26}\text{Mg}$. A simple consideration of kinetic isotope fractionation [6] gives exactly the same slope.

Evaporation, a process that is generally believed to be responsible for isotopic mass fractionation effects in CAIs, follows the Rayleigh equation (derived in [7]):

$$\frac{\left(^{25}\text{Mg}/^{24}\text{Mg} \right)_{\text{residue}}}{\left(^{25}\text{Mg}/^{24}\text{Mg} \right)_{\text{start}}} = f^{\alpha-1}, \text{ and similarly for } ^{26}\text{Mg}/^{24}\text{Mg},$$

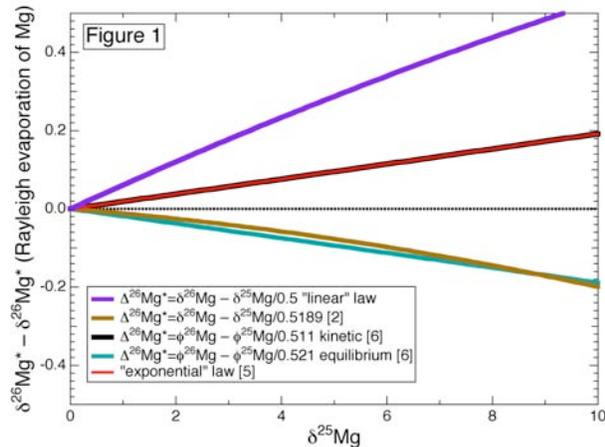
where f is the fraction remaining of the initial ^{24}Mg and α is the gas-solid isotopic fractionation factor. Thermodynamic calculations [8] and experiments [9] show that most of the magnesium evaporates as Mg atoms. The theoretical expectation is that α should be

$$\frac{\gamma_1}{\gamma_2} \sqrt{\frac{m_2}{m_1}},$$

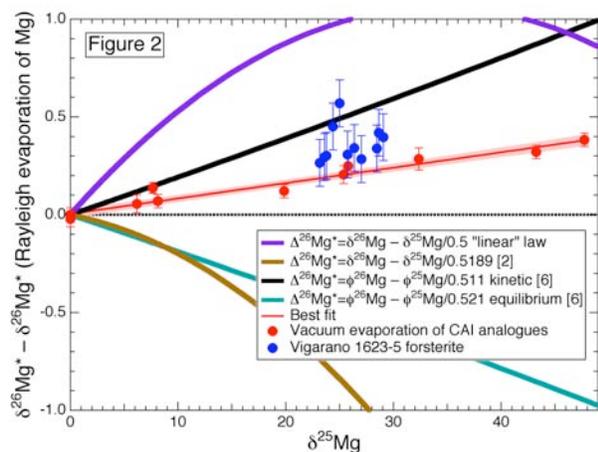
where the γ_1 and γ_2 are evaporation coefficients and m_1 and m_2 are the masses of a pair of isotopes. Assuming that all isotopes have the same evaporation coefficients and using the exact masses for the magnesium isotopes, the Rayleigh equation is linear with a slope of 0.5160 on a plot of $\phi^{25}\text{Mg}$ vs. $\phi^{26}\text{Mg}$. Finally, a simple derivation of expectations for equilibrium isotopic fractionation [6] gives a slope of 0.5210 on a plot of $\phi^{25}\text{Mg}$ vs. $\phi^{26}\text{Mg}$.

The different fractionation laws are compared in Fig. 1, where deviations from Rayleigh fractionation of Mg atoms are plotted vs. $\delta^{25}\text{Mg}$. It can be seen that for typical $\delta^{25}\text{Mg}$ values for CAIs of 5–10 ‰, the different laws give $\Delta^{26}\text{Mg}^*$ values that have a range of several tenths of a ‰. For samples with low Al/Mg ratios, the law used significantly affects inferred $^{26}\text{Al}/^{27}\text{Al}$ ratios.

Experiments. For the last several years we have been conducting vacuum evaporation experiments on melts of Type B CAI bulk composition and measuring the magnesium



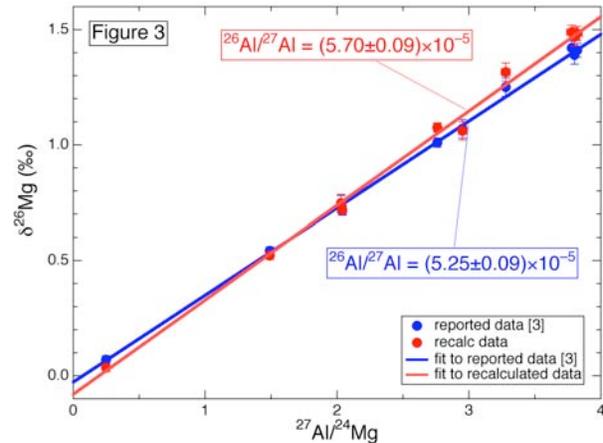
isotopic compositions by solution MC-ICPMS. The high precision isotopic analyses allow a test of the various fractionation laws that are in use. Recent magnesium isotopic data [10] are plotted in Fig. 2. It can be seen that they are well correlated. On a plot of $\phi^{25}\text{Mg}$ vs. $\phi^{26}\text{Mg}$, they lie along a straight line with a slope of 0.51400 ± 0.00024 . The data clearly differ from the line expected for Rayleigh evaporation of Mg atoms and also from all other fractionation laws commonly used. Also shown in Fig. 2 are multicollector ion microprobe data for magnesium from the FUN CAI Vigarano 1623-5 [11].



Since this is a FUN CAI, there is no requirement that the data have an intercept of 0 ‰, but the slope is entirely consistent with slope determined from evaporation experiments.

Implications for ^{26}Al in the solar system. For the amount of magnesium mass fractionation in typical CAIs, the choice of mass fractionation law results in shifts of a few tenths of a ‰. These shifts are independent of Al/Mg ratio and

thus for high Al/Mg ratios, do not significantly affect inferred $^{26}\text{Al}/^{27}\text{Al}$ values. For low Al/Mg ratio, the correct choice of mass fractionation law is critical. Recent studies have argued for a somewhat higher initial solar system ^{26}Al value. We give one example of the effect of fractionation law here. Analyses of chips and whole rock CAIs gave a remarkably precise isochron corresponding to $(5.25 \pm 0.10) \times 10^{-5}$ [3]. These data were corrected with the exponential law [5] (M. Bizzarro, pers. comm.). Recalculating the data with our recommended law changes the inferred $^{26}\text{Al}/^{27}\text{Al}$ value from $(5.25 \pm 0.09) \times 10^{-5}$ to $(5.70 \pm 0.09) \times 10^{-5}$ (Fig. 3).



Conclusion. It is now clear that in the new era of high precision magnesium isotopic analysis by multicollector methods, it is essential to state what fractionation law is used to correct data for natural isotopic mass fractionation. When comparing data between different laboratories, it is highly desirable to use the same mass fractionation law. Since CAIs quite likely became mass fractionated by evaporation, we recommend that data be corrected using a slope of 0.5140 on a plot of $\phi^{25}\text{Mg}$ vs. $\phi^{26}\text{Mg}$.

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