LARGE $^{48}$Ca ANOMALIES ARE ASSOCIATED WITH $^{50}$Ti ANOMALIES IN MURCHISON AND MURRAY HIBONITES

ERNST K. ZINNER, ALBERT J. FAHEY, JITENDRA N. GOSWAMI, TREVOR R. IRELAND, AND KEVIN D. MCKEEGAN

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ABSTRACT

The calcium isotopic compositions of eight individual hibonites from the carbonaceous chondrites Murchison and Murray have been measured in the ion microprobe. Previous ion probe Ti isotopic measurements of the same grains had revealed $^{50}$Ti anomalies with $\delta^{50}$Ti ranging from $-50$ to $+104\%$ (parts per thousand). All hibonites show large $^{48}$Ca anomalies with $\delta^{48}$Ca values from $-46$ to $+56\%$. No resolvable anomalies are seen in $^{42}$Ca and $^{43}$Ca; $^{46}$Ca was not measured. The $^{48}$Ca effects are qualitatively correlated with the $^{50}$Ti effects in the sense that the $\delta^{48}$Ca and $\delta^{50}$Ti values have the same sign. These results confirm the previous conclusions concerning the presence of a nucleosynthetic component produced by neutron-rich nuclear statistical equilibrium processes originally indicated by the Ca, Ti, and Cr compositions of the FUN inclusions EK-1-4-I and C-1; however, they extend the association of $^{48}$Ca and $^{50}$Ti effects to single mineral phases and greatly exceed the magnitude of the FUN anomalies. The $\delta^{48}$Ca/$\delta^{50}$Ti and $\delta^{50}$Ti/$\delta^{46}$Ti ratios of two Murray grains with the largest $^{48}$Ca and $^{50}$Ti excesses agree well with predictions of the multi-zone mixing e-process model published by Hartmann, Woosley, and El Eid in 1985. The results point toward the preservation of the isotopic anomalies with interstellar dust grains as carriers of the $n$-rich Ca and Ti components. The large variation in the $\delta^{48}$Ca/$\delta^{50}$Ti ratios indicates multiple nucleosynthetic components and/or chemical fractionation between Ca and Ti prior to hibonite formation.

Subject headings: abundances — meteors and meteorites — nucleosynthesis — solar system: general

I. INTRODUCTION

This Letter reports ion microprobe measurements of the Ca isotopic compositions of eight individual hibonite (CaAl$_2$Mg$_3$Ti$_2$O$_{19}$) grains from the CM chondrites Murray and Murchison. Previous ion probe measurements of the same grains have revealed large $^{50}$Ti anomalies (Fahey et al. 1985, 1986; Ireland, Compton, and Heydegger 1985, hereafter ICH). In addition to Ti isotopes, Mg isotopes as well as rare earth elements (REE) and other trace elements have been measured in the hibonites for which Ca measurements are reported here (Fahey et al. 1986; Ireland, Compton, and Esat 1986; Ireland, Esat, and Compton 1986; Ireland et al. 1986).

A variety of Ca isotopic anomalies has been observed in primitive meteorites (Lee, Panastasiou, and Wasserburg 1978, hereafter LPW; Lee, Russell, and Wasserburg 1979, hereafter LRW; Niederer and Panastasiou 1984, hereafter NP; Jungck, Shimamura, and Lugmair 1984, hereafter JSL; Prombo and Lugmair 1986, hereafter PL). Effects in $^{48}$Ca are, in many cases, associated with $^{50}$Ti anomalies in Ca-Al rich inclusions (JSL; PL); and are prominent in the FUN inclusions C-1 and EK-1-4-1 (LPW; Niederer, Panastasiou, and Wasserburg 1980, 1981, hereafter NPW 1980, NPW 1981). While the ion probe has previously been used for the measurement of Ca mass-dependent isotope fractionation effects (Hinton, Grossman, and McPherson 1984; Hinton, Davis, and Scatena-Wachel 1985; Hinton and Davis 1986; Fahey et al. 1986), the first ion probe Ca isotopic measurements that include $^{48}$Ca are reported here.

II. SAMPLES, EXPERIMENTAL PROCEDURES, AND RESULTS

The meteorite samples have been described by Fahey et al. (1985, 1986) and ICH. Terrestrial standards consisted of calcite (CaCO$_3$), perovskite (CaTiO$_3$), and Madagascar hibonite.

Previously, Fahey et al. (1985, 1986) described Ti isotopic measurements with the Washington University (WU) Cameca IMS 3F ion microprobe under high mass resolution conditions which allowed the separation of the $^{48}$Ti$^+$ and $^{46}$Ca$^+$ peaks. Ireland, Compton, and Heydegger (1985) used a similar mass resolution for Ti isotopic analyses with the SHRIMP ion probe. The Ca measurements presented here were made at WU under the same high mass resolution conditions as employed for the Ti measurements. These conditions limit the $^{46}$Ca$^+$ interference to less than $10^{-4}$ of the $^{48}$Ti$^+$ signal. The converse is not true since in hibonite and perovskite the $^{48}$Ti$^+$ signal is 10–50 times the $^{46}$Ca$^+$ signal. The interference of the tail of the $^{48}$Ti$^+$ peak with the $^{48}$Ca$^+$ signal was determined by monitoring the high-mass edge of the $^{45}$Ca$^+$ peak at a distance $\Delta m_{40} = 40/48 \times \Delta m_{48}$ from the center of $^{40}$Ca$^+$ peak where $\Delta m_{48} = 4.58 \times 10^{-3}$ amu is the mass difference between $^{40}$Ti and $^{48}$Ca.
The isotopes $^{40}\text{Ca}$, $^{42}\text{Ca}$, $^{43}\text{Ca}$, $^{44}\text{Ca}$, and $^{48}\text{Ca}$ were measured by an automatic peak jumping routine (Fabey et al. 1986). The $^{46}\text{Ca}$ was not measured because of the large unresolved $^{46}\text{Ti}$ interference. Peak centering was performed on all the measured Ca isotopes except for mass 48 where it was done on $^{48}\text{Ti}$++. The $^{46}\text{Ca}$ signal was then measured by jumping from the $^{48}\text{Ti}$++ peak to a magnetic field corresponding to the $^{48}\text{Ca}$ mass. In the calcite standard the Ti concentration was negligible and peak centering was done on $^{48}\text{Ca}$++. In the terrestrial hibonite standard a correction was made for the $^{88}\text{Sr}$+++ and $^{86}\text{Sr}$+++ interferences to $^{43}\text{Ca}$++ and $^{44}\text{Ca}$++ by measuring $^{87}\text{Sr}$++. In all meteoritic hibonites the Sr+++ contributions were checked and found to be negligible (less than 0.1%).

The results are given in Table 1. Data are reported as per mil (‰) deviations ($\delta$-values) of the isotopic ratios relative to $^{44}\text{Ca}$ from the terrestrial values given by NP after an exponential mass fractionation correction with $^{40}\text{Ca}$ as the secondary reference isotope.

Measurements on the calcite yield normal values. The validity of the $^{48}\text{Ti}$ interference correction is demonstrated by the fact that the Ca isotopic composition measured in the terrestrial perovskite and hibonite standards is normal within the errors. In contrast, the meteoritic hibonites show large $^{48}\text{Ca}$ anomalies with $\delta$-values ranging from $-46\%$ in MUR-20 to $56\%$ in MY-H4. No anomalies are resolvable for $^{42}\text{Ca}$ and $^{43}\text{Ca}$. No special effort was made to measure the intrinsic mass fractionation since the instrumental mass fractionation is affected by the condition of the sample surface and all meteoritic hibonite grains had been extensively sputtered during the analysis of Mg and Ti isotopes and REE.

III. DISCUSSION

The most striking results of the present measurements are the large $^{48}\text{Ca}$ anomalies which are two orders of magnitude larger than those observed in normal inclusions (NP; JSL; PL) and at least a factor of 4 larger than in the FUN inclusions (LPW). The $^{48}\text{Ca}$ anomalies are qualitatively correlated with the $^{50}\text{Ti}$ anomalies in the sense that the signs of the $\delta^{48}\text{Ca}$ and $\delta^{50}\text{Ti}$ values are the same (Fig. 1). Previous thermal ionization mass spectrometric measurements of Ca and Ti in the FUN inclusions C-1 and EK-1-4-1 have shown the same correlation (LPW; NPW 1980; NPW 1981). While neutron-rich Si-burning (Cameron 1979), the $\eta$-$\beta$ process (Sandler, Koonin, and Fowler 1982), and the neutron-rich nuclear statistical equilibrium (NSE) process (Cameron 1979;
Hartmann, Wooley, and El Eid (1985, hereafter HWE) can produce the $n$-rich isotopes $^{48}$Ca and $^{50}$Ti, the association of $^{54}$Cr excesses with $^{50}$Ti excesses in normal Allende CAIs (Birck and Allègre 1984; Papanastassiou 1986), and especially the $^{54}$Cr excess accompanying $^{48}$Ca and $^{50}$Ti excesses in EK-1-4-1 (Papanastassiou 1986), effectively rule out the first two processes.

In order to compare our results with NSE predictions a discussion of the observed $^{48}$Ca and $^{50}$Ti anomalies is necessary. Fahey et al. (1986) have presented arguments which indicate that the hibonite grains formed in the solar nebula. The Ca isotopic data do not alter this conclusion, and all our interpretations of the Ca and Ti isotopic anomalies are made within this framework.

The $^{48}$Ca and $^{50}$Ti anomalies (Fig. 1) are neither consistent with only the addition of an exotic component to material of solar system isotopic composition, nor with simple mixing between two end-members. It is likely that we are dealing with multiple distinct components. Although the excesses of $^{48}$Ca and $^{50}$Ti can be identified as being due to NSE processes, different conditions, such as different neutron excesses in the stellar zones where these processes take place, can result in markedly different $^{48}$Ca/$^{50}$Ti production ratios (HWE). The $^{48}$Ca and $^{50}$Ti deficits are not necessarily the result of a single nucleosynthetic process since many different processes can contribute to the production of the other Ca and Ti isotopes. In fact, a statistical analysis of Ti isotopic data alone previously provided evidence for the presence of at least four nucleosynthetic components in solar system Ti (Fahey et al. 1986).

The distribution of data points with excesses and deficits in Figure 1 is then explained as due to mixtures of one or more end-members rich in both $^{48}$Ca and $^{50}$Ti with material depleted in these isotopes with respect to the solar composition (solar is itself a mixture of material from several nucleosynthetic sources). The number and composition of the end-members are unknown. The mixing of a large number of end-members with diverse compositions could lead to populating the $^{48}$Ca-$^{50}$Ti plane fairly uniformly. However, the fact that all CM hibonite points, as well as those for C1 and EK-1-4-1, lie in two quadrants indicates the dominance of a component with positively correlated $^{48}$Ca and $^{50}$Ti and also indicates that the end-members preferentially mixed with material of a nearly solar system isotopic composition. Still, the mixing of compositions lying far out in the $^{48}$Ca-$^{50}$Ti rich and poor quadrants in Figure 1 can lead to opposite signs of $^{48}$Ca and $^{50}$Ti. This may be the case for HAL hibonite (LRW; Fahey et al. 1986) which could have been produced by the mixing of compositions close to MY-H3 and MUR-20. Likewise, the compositions of the samples MUR-H8 and EK-1-4-1 could have been the result of mixing of compositions close to those of MY-H3 and MUR-170. In addition to mixing, there is the possibility of chemical fractionation of Ca from Ti in the interstellar medium before mixing with solar system material which would lead to a redistribution of points within a quadrant of the $^{48}$Ca-$^{50}$Ti plane.

Because of all the above complications, we have to make certain assumptions in order to compare our results with theoretical predictions, specifically those of the multizone mixing (MZM) NSE model of HWE. Only points with $^{48}$Ca
and $^{50}$Ti excesses are compared (for the $n$-deficient points there is no simple theoretical framework on which to base a comparison); the excesses are assumed to result from the addition of $n$-rich components to solar system material. We also assume that no presolar chemical fractionation between Ca and Ti took place.

The presentation of Figure 1 where $\delta^{46}$Ca is plotted versus $\delta^{50}$Ti also assumes that the original carriers of the anomalous Ca and Ti were mixed with a reservoir of solar Ca/Ti elemental ratio. This is reasonable since there is no evidence for preserved carrier dust grains in the hibonites and the REE patterns indicate condensation from a gas of solar composition at high temperature (Fahey et al. 1986). Also plotted in Figure 1 are lines of different ($^{46}$Ca/$^{48}$Ca)$_0$/$^{50}$Ti/$^{50}$Ti$_0$) ratios predicted for various values of the maximum neutron excess, $\eta_{\text{max}}$, of the MZM model. The $\delta^{46}$Ca/$\delta^{50}$Ti ratios measured in the hibonites vary by an order of magnitude, possibly reflecting a range of $\eta_{\text{max}}$ in different sources or incomplete mixing of zones with different $\eta$ from a single supernova. The $^{46}$Ca and $^{50}$Ti excesses measured in the grains MY-H3 and MY-H4 are consistent with the MZM model for values of $\eta_{\text{max}}$ between 0.16 and 0.17. This range also agrees well with respect to the $\delta^{50}$Ti/$\delta^{46}$Ti ratio: the MZM predictions are 25.8 for $\eta_{\text{max}} = 0.159$ and 20.5 for $\eta_{\text{max}} = 0.171$ (Hartmann 1986) while the measured ratios in MY-H3 and MY-H4 are $25.7^{+0.4}_{-0.7} \text{ and } 27.4^{+0.2}_{-0.7}$ (1 $\sigma$) respectively. The fact that both the $\delta^{50}$Ti/$\delta^{46}$Ca and $\delta^{50}$Ti/$\delta^{46}$Ti ratios are consistent with a single value for $\eta_{\text{max}}$ indicates that, given the above mixing model, chemical fractionation between Ca and Ti must have been small for the carriers of the anomalous Ca and Ti in these two hibonites.

The $\delta^{46}$Ca/$\delta^{50}$Ti ratios in MUR-H7, MUR-H8, and EK-1-4-1 require a much higher $\eta_{\text{max}}$ value of $\sim 0.20$. The corresponding decrease in $\delta^{50}$Ti/$\delta^{46}$Ti generally agrees with the values of $3.4^{+1.5}_{-1.3}$ for MUR-H7 and $2.0 \pm 0.1$ for EK-1-4-1 but we presently lack precise MZM predictions for $\eta_{\text{max}} = 0.20$.

The presence of nuclear anomalies in Ca could lead to systematic errors of several per mil in the $^{46}$Ca corrections made for low mass resolution ion probe measurements of Ti isotopes in hibonites. While $^{46}$Ca$^+$ and $^{46}$Ti$^+$ were separated during the Ti measurements of Fahey et al. (1985, 1986), a correction for $^{46}$Ca$^+$ was made for the $^{46}$Ti$^+$ measurement. The magnitude of a systematic error made on $^{46}$Ti depends on the size of a possible $^{46}$Ca anomaly. The MZM predictions are $\delta^{46}$Ca/$\delta^{48}$Ca = 1.0 $\times$ 10$^{-2}$ for $\eta_{\text{max}} = 0.159$ and even less for higher values of $\eta_{\text{max}}$ (Hartmann 1986). For MY-H3 the predicted value of $\delta^{46}$Ca would be only 0.5% resulting in a correction to $^{46}$Ti of 0.04% which is completely negligible. In EK-1-4-1 the measured $\delta^{46}$Ca/$\delta^{48}$Ca ratio is 0.24 (NP) which is much higher than the MZM prediction, possibly due to $\nu$-process contributions to the $^{46}$Ca abundance. Even with the $\delta^{46}$Ca/$\delta^{48}$Ca of EK-1-4-1, the error to the correction for MY-H3 is only 0.1%.

The correlated $^{46}$Ca and $^{50}$Ti anomalies of the present study raise questions concerning their preservation between production of these isotopes in specific nucleosynthetic sites and their incorporation into the solar nebula. Previously, these questions were addressed by Niemeyer and Lugmair (1984, hereafter NL) and Fahey et al. (1986) in connection with the multiplicity of Ti isotopic components and by JSL in discussing correlated $^{46}$Ca and $^{50}$Ti anomalies. The above authors argued for a "chemical memory" (Clayton 1982) origin of the observed effects, where the chemical nature of solid carrier phases containing products from distinct nucleosynthetic sources, as well as their reprocessing in interstellar space and the early solar nebula, led to the preservation of exotic isotopic signatures (see NL for a more thorough discussion). In contrast, Hinton, Davis, and Scatena-Wachell (1987) construed the lack of correlations between $^{50}$Ti anomalies in hibonites and their chemical compositions as well as isotopic mass fractionation as evidence against the chemical memory model and, instead, argued for a late supernova injection of exotic material into the solar nebula. However, the qualitative correlation between $^{50}$Ti and $^{46}$Ca effects displayed in Figure 1, coupled with the lack of any correlation of these anomalies with the presence of radiogenic $^{26}$Mg (Fahey et al. 1986), strongly favors a chemical memory origin. Fahey et al. (1985, 1986) have pointed out that in all likelihood the hibonites themselves are not identical with the carrier grains which preserved the isotopic anomalies. If this is the case then most chemical properties, such as REE patterns and probably isotopic mass fractionation effects observed in the hibonites, are determined by the physicochemical conditions of the reservoirs in which the hibonites formed, while "nonlinear" isotopic effects (such as $^{46}$Ca and $^{50}$Ti anomalies) were preserved in presolar grains which were evaporated but incompletely mixed with material of normal isotopic composition before condensation of the hibonites. Such a scenario implies very localized processes occurring in the solar nebula on a short time scale (Boynton 1978; Wark 1985; Wood 1985).

Concerning the nature of the carriers, Clayton (1981) considered condensation of $^{50}$Ti into metal grains in supernova ejecta. On chemical grounds, it is not clear whether Ca condenses into these metal droplets, and refractory oxide grains are more likely carriers for the correlated exotic Ca and Ti. Although the exact nature of the carrier grains remains unknown, the correlated isotopic effects indicate that the processing of original circumstellar grains in the interstellar medium and solar nebula has not completely obliterated their isotopic record.

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ALBERT J. FAHEY, KEVIN D. MCKEEGAN, and ERNST K. ZINNER: McDonnell Center for the Space Sciences, Campus Box 1105, Washington University, St. Louis, MO 63130

JITENDRA N. GOSWAMI: Physical Research Laboratory, Navarangpura, Ahmedabad 380 009, India

TREVOR R. IRELAND: Research School of Earth Sciences, The Australian National University, Canberra ACT 2601, Australia

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