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Scale update: WMO CO_X2025 - January 2026

1. Introduction

The WMO carbon monoxide in air mole fraction scale has been updated and the scale range has been increased to cover the nominal mole fraction range 25-1000 ppb. The new scale (WMO CO_X2025) updates the X2014A scale to better account for the drift in the current primary standards (in use since 2011) and to improve assignments to older primary and secondary standards that defined the CO scale from 1993 through mid-2011. This revision follows on the presentation and discussion at GGMT-2024 (Hall et. al, 2024).

All CO tank calibration measurements from 1993 – present have been reprocessed from the original raw data using the new assignments for standards on the CO_X2025 scale. Revised results for each calibration episode are available on the CCL website (<https://gml.noaa.gov/ccl/>) Raw data for measurements made before 1993 are not available and their results have not been revised.

2. Analytical methods

Four analytical methods were used by the CCL to transfer the CO mole fraction scale to standards prepared for the community (see table 1): gas chromatography with hot mercuric oxide reduction followed by resonance absorption detection of the resulting Hg vapor (GC_HgO) (Novelli et al., 1991), vacuum ultraviolet resonance fluorescence spectroscopy (VURF) (Gerbig et al., 1999), off-axis integrated cavity output spectroscopy (OA-ICOS) (Baer et al., 2002), and quantum cascade-tunable infrared laser direct absorption spectroscopy (QC-TILDAS) (McManus et al., 2015). The optical methods (VURF, ICOS, and QC-TILDAS) greatly improved measurement performance over the GC_HgO technique. Typically, all instruments were calibrated using multiple standards to define a response curve to relate instrument response to a mole fraction with the exception of the VURF instruments used from 2003-2009 which were calibrated by a single standard between 300 – 400 ppb and a zero. Instruments were typically calibrated over the nominal range 50-200 ppb from 1993 - 1999, 50-350 ppb from 2000-2005, 25-500 ppb from 2010-May 2014, and 25-1000 ppb since. The CCL often overlapped analytical methods when transitioning to new methods. Typically, during overlap periods a single “official” method was used for CCL issued certificates but all results are now shown on the CCL website.

Instruments are designated as official calibration instruments by a time dependent lookup table in the reftank database (table reftank.inst_status). This allows tank air measurements on flask systems or test instruments to be excluded from release until the CCL has confidence in the new method.

3. Calibration episode uncertainty

Uncertainties for CO calibration episodes are determined as described for other species as scale transfer uncertainty (link to doc) with the exception that due to the complexity of maintaining the CO scale there is no distinction made between total and scale transfer uncertainty.

The uncertainty of a measurement episode is calculated from the uncertainty of the calibration curve used to relate instrument response to mole fraction, the repeatability of the instrument, the long term reproducibility of the instrument type, and any additional type B uncertainty terms required. The combined standard uncertainty is given on the website and in figures here unless an expanded combined standard uncertainty is indicated.

4. Overview of the WMO CO scale

4.1. 1993 through June 2011

Due to the lack of stability of CO in air mixtures stored in high pressure aluminum cylinders, the CO scale has not been maintained with the same methodology as other trace gas species maintained by the CCL at NOAA. The scales for other species are typically embodied by a single set of stable primary standards that are used over decades to provide a consistent scale. The potential for growth of CO in cylinders means that the initial assigned values placed on gravimetric standards cannot be considered valid after some period of time. Typically, CO growth becomes significant after 1-2 years (see section 8 below). Because of this, the CO scale prior to mid 2011 was defined by repeated sets of gravimetric standards made every few years which are linked by common secondary standards. Secondary standards were directly calibrated by the gravimetric sets before growth in the gravimetric standards became significant or after the application of an independently derived drift assessment to the gravimetric standards. The secondary standards tie the scale together across multiple gravimetric sets made years apart.

The CO scale from 1993 through mid-2011 is defined by seven sets of gravimetric standards (prepared in 1992, 1996, 1997, 1999/2000, 2006, 2011, and 2015). Each set (except the 1992 set) is used to value assign the secondary standards used to implement the scale soon after production (figure 1). An earlier set of gravimetric standards (made in 1988/1989) are not included in the definition of the CO_X2025 scale. These 1988/1989 standards were made in small 5.9 L cylinders and exhibited fast growth of CO (subsequent sets were prepared in 29 L cylinders that exhibit much slower growth rates). The results of calibrations against them are suspect because of the rapid drift rates and the raw instrument data is no longer available for further inspection.

The 1992 set of gravimetric standards was comprised of only 3 standards so did not cover the full range of the scale. They were used mainly as a diagnostic for the 1988/1989 gravimetric standards and then turned into working standards to calibrate the instruments going forward. We treat these as "secondary" standards in that they were used routinely with other secondary standards in the 1990s to calibrate the instrument response and value assign tertiary standards.

Note, the 2006 set of gravimetric standards was only used to value assign the secondary standard in service at that point in time (CA03516). This set was unfortunately not used to evaluate any of the prior primary or secondary standards.

Also, note that measurements against the “freshly made” 2015 gravimetric standards were used to value assign primary and secondary standards in use prior to 2011 but are not used for the 2011 primary standards assignments. This follows decisions made for the 2014A scale due to the fact that the pre-2011 standards were not measured directly against the 2011 primary standards (or by the internal tracer method) at that point in time. The 2015 episode was therefore needed to confirm drift rates in pre-2011 standards.

Prior to mid-2011, the transparency of the CO scale traceability chain is complicated for several reasons. Not all secondary standards were measured against all gravimetric sets resulting in different traceability paths for secondary standards used concurrently. In addition, the traceability path is further complicated by the practice of converting gravimetric standards into the role of a working standard and using them along with secondary standards to routinely calibrate the instruments over time. This confuses the definition of primary, secondary, and tertiary level standards we're accustomed to.

Many of the historical primary and secondary standards used from 1992-2011 have been re-measured since the X2014A scale release and these new measurements are used to improve the consistency and traceability of the CO scale prior to 2011.

4.2. July 2011 - present

In 2011, the CCL changed the method used to define the CO scale to improve transparency and long-term (decadal) consistency of the scale. The 2011 gravimetric standards were designated as the primary CO standards with the intention of using this single set of standards to define the scale over time. There are 14 2011 gravimetric standards, referred to in this document as the 2011 primary standards, covering the nominal range 25 – 1000 ppb CO (see Table 2). Secondary standards (and therefore all tertiary standard measurements) are traceable only to this single set of primary standards through a strict hierarchy since July 2011 (the date at which the current secondary standards went into service).

The 2011 primary standards are drifting upwards, as typical for air mixtures stored in aluminum cylinders, which would lead to biased results for tertiary standards calibrated by the CCL if not accounted for. Therefore, an internal tracer method was developed to track growth of CO in the primary standards. This method takes advantage of the stability of the WMO/NOAA CH₄ scale and the assumption that CO growth in cylinders is likely a wall effect and is not mole fraction dependent.

In 2013/2014, three very high mole fraction gravimetric mixtures of CO and CH₄ in air were made in 5.9 L aluminum Luxfer cylinders. These "parent" tanks contain 0.1 – 1% CO and ~ 3% CH₄ (see Table 3). They were made gravimetrically such that the CO:CH₄ ratio is known with small uncertainty. Typical growth rates of CO in these small aluminum cylinders, up to a few ppb per year, is insignificant compared to the amount of CO in the parent tanks giving a stable CO:CH₄ ratio. Static dilutions from the parent tanks are made by blending small aliquots of parent gas with scrubbed zero air in 5.9 L aluminum Luxfer cylinders. By varying the size of the parent aliquot and the amount of diluent gas, various CO mole fractions can be targeted to cover the same mole fraction range as the 2011 primary standards. The CH₄ mole fractions in these "dilution" standards are measured relative to the WMO CH₄ scale and used with the known CO:CH₄ ratio of the parent tank to assign a CO value to the dilution standard (correcting for CH₄ and CO blanks in the diluent gas as needed).

Dilution standards can be made consistently over time from the stable parent tanks (uncertainties range from 0.2 to 1.2 ppb, 68% confidence intervals). Suites of 12-16 dilution standards are made on one day and analyzed within 1-2 days to calibrate an instrument response curve and measure the primary CO standards. This can be done multiple times per year if necessary due to the simplicity of making these standards compared to gravimetric standards. In the beginning, we made sets of dilution standards to calibrate the 2011 primary standards 2-3 times per year to evaluate the method but now schedule these episodes for approximately once every 12-18 months due to time limitations on CCL personnel. Results from these episodes allows the CO rate of change in the primary standards to be determined. As an example, Table 4 lists the dilution standards made for the August 2015 calibration episode. The uncertainty budget of the dilution standards includes CO and CH₄ in the diluent gas (it is passed through a 430 g Sofnocat trap so the assumed CO in the diluent is 0 ± 0.2 ppb, while the CH₄ is measured with values typically ranging from less than the analyzer detection limit of ~2 ppb to 5 ppb), uncertainty of the gravimetric CO:CH₄ ratio of the parent, and the total uncertainty of the CH₄ measurement on the WMO CH₄ scale.

At GGMT-2015 we described the internal tracer method, and the X2014A scale revision was released shortly thereafter (in December 2015). The drift corrections applied to the 2011 primary standards for the X2014A scale revision were based on the initial gravimetric value for each primary standard plus the average of the first 5 measurement episodes available at that time using the internal tracer technique. Drift rates assigned to the primary standards ranged from 0 to 1 ppb/year.

We have continued measuring the 2011 primary standards using the internal tracer technique and updated assessments were presented at GGMT-2017 and GGMT-2024. Since the X2014A scale release, the internal tracer technique measurements have shown that drift rates applied to the 2011 primary standards for X2014A were often too large. This introduced a time-dependent positive bias in the primary standards as indicated by the difference between the X2014A assignments and the recent measurement results of the primary standards (See measurements with the internal tracer method in Figure 2). With the X2025 scale revision we aim to correct these mis-assignments using all available data through the most recent

calibration episode performed in December 2025 and improve the time and mole fraction consistency of the scale dissemination.

5. X2025 Value Assignments of the 2011 primary standards

The CCL has been aware of the mis-assignment of the X2014A drift corrections applied to the 2011 primary standards since ~2017 as additional internal tracer method episodes extended the 2011 primary standards measurement records. A major complication in correcting the drift assessments of the 2011 primary standards has been the observed offset between the gravimetric value for the standards and the initial value which would be inferred from the linear fit of the internal tracer method measurements alone (Figure 2). The now 12-year measurement records using the internal tracer technique required either an initial non-linear drift in some of the primary standards (best visible at the low end of the scale) else the initial gravimetric values were not consistent with the internal tracer method. Only recently have we been able to reconcile this discrepancy with confidence. We discuss this in detail here before discussing the broader scale implementation in the next section.

To evaluate the consistency of the methods, we made a full set of CO primary standards in 2015 and a smaller set covering a more limited mole fraction range in 2017 using the gravimetric technique. Both of these sets were measured within 2 weeks versus a fresh set of dilution standards made using the internal tracer method. Figure 3 show the differences and uncertainties determined with the two techniques. The measured values for the gravimetric standards determined from the internal tracer technique in both validation studies are within the 68% confidence interval (CI) of the gravimetric value for all but two and well within the 95% CI for all of the gravimetric standards. These results gave us confidence that the internal tracer technique developed and implemented by the CCL agrees well with the more established gravimetric technique.

We trust results using the internal tracer method, therefore we consider two possible causes of the discrepancy. Either the 2011 gravimetric value assignments have an error or the rate of CO growth in the cylinders is not constant. We can now use the 2015 gravimetric standards to demonstrate that the offset is most likely due to initial nonlinear growth of CO in the cylinders.

We have continued to monitor the 2015 gravimetric standards using the internal tracer method to serve as a backup set of primary standards with well characterized drift rates (in case something happens to the 2011 primary standards) and to better understand the viability of the internal tracer technique for maintaining the scale. The measurements over the past ten years show these standards are drifting slowly upwards over time. We also see a period of quicker drift over the first 1-2 years after production, followed by a slower linear growth that continues through the most recent measurements (Figure 4). This gives us confidence that this behavior is possible and is the most likely cause of the offset seen in the 2011 primary standards when comparing the 2014-2025 measurement histories with their gravimetric values.

As a practical way to model the initial CO growth rate with our current data processing code, we approximate the drift observed in the 2011 primary standards with a value assignment based on a 2nd order polynomial of the gravimetric value plus the measurement results using the internal tracer method through the end of 2017. This initial value assignment is then followed by second value assignment based on a linear fit to only the measurement results from the internal tracer method from 2016 through 2025. This allows us to extrapolate forward in time as a linear function. The split fit for 2011 primary standard CA08161 is shown in Figure 5. One disadvantage of this split value assignment is that a small discontinuity (less than ~ 0.5 ppb for most) results when the change occurs in June 2016. However, the changeover date was chosen to minimize this and it has only a small effect on the implemented scale. Calibration histories of all the 2011 primary standards and the split value assignments derived for them are included in the supplemental figures. Table 5 lists value assignments for 2011 primary standards which define the X2025 scale from mid-2011 through present.

6. Traceability of X2025 scale revision

The X2025 scale revision includes all measurements of current and archived primary and secondary standards up to December 2025. Here we start our discussion with the recent period (July 2011 - present) and then move through the more historical time periods where we describe our work to improve consistency and transparency of the implementation.

In general, the CCL attempts to maintain a strict hierarchy of calibrations to ensure measurements are fully traceable. Primary standards are value assigned based on the initial gravimetrically determined value plus subsequent measurements against future independent sets of gravimetric standards or measurements using the internal tracer method. Secondary standards are value assigned using measurements vs primary standards (either soon after the primary standards were produced or after the primary standards have had their drift rates determined through measurements). There are a few exceptions as will be noted below.

Descriptions roughly follow three analytical system and calibration strategy periods (2011 - present, 2000 - 2010, and 1992-1999) back in time with some overlap. The details are included to document the decisions made to ensure consistent scale implementation. Additional figures and tables are included in the supplemental material to maintain full transparency.

6.1. 2011 - present

In the current hierarchy employed by the CCL, the scale is transferred from the 2011 primary standards to secondary standards to minimize use of the primaries and extend their lifetimes. The CCL has used a single set of 11 secondary standards (produced by Scott Marrin, USA, in N265 sized Luxfer aluminum cylinders) for CO calibrations since July 2011 (with the small

exception that two of the 11 members were added in 2014 to extend the range from 500 ppb to 1000 ppb). These secondary standards have been value assigned by calibration against the 2011 primary standards many times during the intervening years. This gives a highly consistent and transparent traceability chain for CCL calibrations since July 2011.

The secondary standards at the lower end of the range show some initial non-linear drift similar to that observed in the 2011 and 2015 gravimetric standards. We have decided to use the same approach for modeling this behavior by splitting the value assignments of secondary standards below 250 ppb into an initial non-linear function which transitions into a linear function. This prevents the initial non-linear rate of change from affecting the value assignments projected into the future. The initial value assignment is based on a fit to measurement results from 2011 - 2017 and the second value assignment is based on measurements from 2016-2025. The transition is set to June 1, 2016 to match the transition date in the primary standards split assignments. Value assignments for current secondary standards are listed in Table 6, see supplemental for figures.

6.2. 2000 - 2011

The time period from roughly 2000 through 2009 is the most complicated period for documenting the traceability of the scale. It includes the transition in 2004 from analytical systems using the GC-HgO method to a newer gas handling system using the first VURF optical analyzer (Gerbig et al., 1999). This analyzer reduced the uncertainty of the calibrations. It had a much more linear response and was therefore calibrated using a single standard and a zero, assuming linear response over the scale range. The traceability chain was primarily through the 1999/2000 gravimetric standards (listed in Table 7) but there are complexities involved in this and the period is linked to additional measurements made after 2009. However, this period does have a suite of target tanks that went into service in 2001 that allow evaluation of the scale implementation.

The 1999/2000 gravimetric standards were made from August 1999 through February 2000 in 29 L aluminum cylinders. At this point the working standards in use during the 1990s (see section 5.3 below) were at lower pressures so the 1999/2000 gravimetric standards were transitioned into the role of working standards and routinely used to calibrate the RGA instrument from 2000 to 2006 and as the initial working standards on the VURF instrument from 2004 through 2005. Stability assessment and value assignment of these standards is complicated by the lack of independent measurements while they were in service. The first independent measurements of these standards after their time in service was versus the 2015 gravimetric standards in 2015. We began routine measurements of these standards using the internal tracer method beginning in 2018.

Many of the standards on the lower end of the range show indications of more rapid drift early, potentially similar to that observed in the 2011 and 2015 gravimetric standards. However, 1999 gravimetric standard CA03958 (approximately 400 ppb) shows consistent measurement results (vs both the 2015 gravimetric standards and vs standards made using the internal tracer

technique) with the gravimetric value with only a small drift rate (Figure 6). CA03958 is value assigned based on the gravimetric value plus the measurement results and is used to help value assign the other members of the 1999/2000 set. This standard was used as one of the two initial working standard on the VURF analyzer from May 2004 through January 2006 (the other initial standard was CA04007 which shows more rapid CO growth). The other 1999/2000 gravimetric standards were measured relative to CA03958 on this VURF instrument. We include these VURF measurements relative to CA03958 in the value assignment of the other members of the 1999/2000 gravimetric standards set to help constrain the value assignments closer to the time in service. Figure 7 shows an example of one of the other 1999/2000 gravs (serial number CA03973) with the results of calibrations against CA03958 included in the fit. Calibration histories for all 1999/2000 gravimetric standards are shown in the supplemental.

For internal documentation, we note that an additional complexity occurred from 2004 - April 2006 during the initial operation of the first VURF instrument (instrument code V1). During this time period, data acquisition and control software was used that did not conform to typical procedures at the CCL. Electronic data files from this time were recovered years later and converted into standard formats. Some data may have been lost during the file recovery process because the original system stored daily files named as "mmdd.dat" and were overwritten on subsequent years. In addition, the way the CO calibration system was configured resulted in single aliquot calibration episodes during this period. A repeatability term of 0.4 ppb (for mole fractions below 500 ppb) or 0.8 ppb (for mole fractions above 500 ppb) is added in the type B uncertainty lookup table for analysis on instrument V1 from 2004 to April 2006 to account for the lack of multiple aliquots during a calibration episode.

On retirement of the 1999/2000 gravimetric standards in late 2005, the VURF instrument was calibrated using two true secondary standards (CA03516, filled by Scott Marrin around August 2005, in use 2005-12-23 through 2007-09-18; and CA07318, filled by Scott Marrin around October 2006, in use 2007-09-27 through 2009-12-03). CA03516 was value assigned using measurements vs the 1999/2000 gravimetric standards on the VURF prior to use and verses the 2006 gravimetric standards during use (Figure in supplemental). CA07318 had pre-deployment calibrations vs CA03516 and post deployment calibrations several years later versus the 2011 gravimetric standards and we assume a linear drift between these measurements. Measurements against the 2011 secondary standards show that CA07318 did indeed likely drift in a linear fashion but they are not included in the fit (Figure 8).

From October 2009 through January 2011, the CCL had a series of analytical system failures on the CO calibration system. CO calibrations were run on an analysis system typically used to measure discrete air samples using a VURF instrument. However, the calibrations were done relative to secondary standard (CA07318) that was moved from the calibration system to the flask analysis system to preserve the scale traceability chain.

From March 2010 through February 2011, the CCL worked to transition the CO calibration system to a new offaxis-ICOS instrument with full implementation in February 2011. It was recognized that we needed to install a multi-standard calibration strategy at this time. However, the only set of appropriate tanks the CCL had on hand at the time were a subset of long-term target tanks (6 cylinders, covering the nominal range 25 - 300 ppb, filled by Scott Marrin in 2001, see Table 8). These were used from March 2010 through April 2011 when a designated set of secondary standards was obtained. Value assignments of this set of target tanks are based on measurements vs the 2011 primary standards after their deployment as standards.

6.3. 1992 - 1999

CO calibrations from 1992 through 1999 were performed using GC-HgO instruments and the scale was implemented using 11 working standards (listed in Table 9) with 3 to 6 of the 11 picked on any given day to calibrate the analyzers. Three of these working standards are the 1992 gravimetric standards whose values assignments include the gravimetric value while the others are more traditional secondary standards with value assignments solely from calibrations against primary standards. 6 of these working standards have been preserved and have been measured since the X2014A revision. These additional measurements give us more insight into the value assignments of these tanks and form the basis of the revision during this time period (see figures in the supplemental). Two of the 1990s working standards (CC86203 and CC114932) were not well calibrated during the time in use. We apply additional time dependent uncertainty terms to account for a standard being used outside of the time period where we have independent assessments of its value assignment

For internal documentation we note that re-evaluation of this period resulted in a few differences compared to earlier published information: Novelli et al. (2003) indicated 9 secondary/ working standards were in use during this time period. However, the list in this publication includes tank serial numbers that we do not have records of and omits tanks that we feel should have been included based on the raw data files from the period. For the X2025 scale we choose to base the scale on the 11 standards recorded in the datafiles. Also as explained in Novelli et al. (2003), during this time period most calibrations of the secondary standards were relative to other members of the secondary set. The aim was to identify drifting members of the set relative to the other members. For CO where drift is common in aluminum cylinders and can occur at relatively similar rates this technique was not successful at determining drift in the scale itself. We ignore these circular calibration episodes when value assigning the working standards from the 1990s. We limit inclusion in the fitting algorithm to those episodes that are independently traceable to the scale as defined by the independent sets of gravimetric standards and the more recent internal tracer method.

Additionally, electronic data records from 1993 - 2001 were recovered from floppy disk storage around 2010. Recovering these records and putting them into the correct format for current

processing code required identifying standards used and samples measured from paper records and correcting serial numbers of both for missing letter pre-fixes and other typos. This may have led to some differences in what was originally calculated at the time from what eventually ended up in the current database records.

7. Evaluation of the scale revision and its implementation

7.1. Comparison of calibrations on X2025 and X2014A

The effect of the full reprocessing of the scale is shown in Figure 9, where X2025 minus X2014A results for tank calibrations of tertiary standards is plotted vs time. The effect of the lower drift estimates for the 2011 primary standards appears as an increasing positive bias in X2014A calibrations which becomes significant for CO measurements around 2020. Since 2020, the biases in the X2014A scale have grown steadily, especially at the lower end of the scale range. Biases in 2025 have reached +5 ppb at 50 ppb but are near 0 at 500 ppb and approximately -2 ppb at 700 ppb (see Figure 10). Variations in the relationship between the two scales prior to ~2012 are due to subtle changes in the value assignments of the historical standards based on new measurements and on implementing more rigid hierarchy of scale transfer to prevent circular dependencies and improve transparency.

7.2. Evaluation of scale implementation

The CCL has maintained a suite of target cylinders in large (N265) aluminum cylinders, purchased from Scott Marrin, since 2001. The suite has been expanded with additions through 2016 and now covers the nominal range 25 - 1000 ppb. They are routinely measured at the tertiary level of the calibration hierarchy as part of the CCL's on-going quality assurance plan. Figure 11 (and table 10) shows calibration histories for four of the set (the others are available in the supplemental). Assuming drift is occurring in these cylinders, we see very good consistency across instruments and calibration strategy periods since 2001. The average of the residuals of a fit to the calibration histories of target tanks with mole fractions at or below 300 ppb is approximately 0.5 ppb. Residuals are larger at higher mole fractions but are less than 1% up to 1000 ppb. The rate of growth is fairly consistent in these target cylinders over time. Low mole fraction target tanks can show some indication of non-linear growth.

Prior to 2001, we are limited in cylinders that can be used to monitor the consistency of the scale implementation over time. However, the secondary standards in use during the 1990s were inter-calibrated in an attempt to identify drifting members. On the X2025 scale, the results from these inter-calibrations are not used in the value assignments of any of the secondary standards. These results (an example is shown in Figure 13) do however give us some indications that the scale is consistent from the mid 1990s through present.

8. Implementation at external laboratories

We recommend that the X2025 scale revision is implemented at laboratories by obtaining revised calibration data for all laboratory standards measured by the CCL (available at <https://gml.noaa.gov/ccl/>) and reprocessing. Drift in the standards, determined by re-calibrations at the CCL or by other lab specific procedures, should be corrected during the reprocessing. This is the most reliable way to account for the time and mole fraction dependent bias in the CO scale that have developed since the release of X2014A and to maintain traceability to the WMO CO scale.

Going forward we suggest that labs follow the GGMT recommendations and have the highest level laboratory standards re-calibrated by the CCL every three years to actively maintain traceability to the scale. Currently, only around 30% of the CO standards produced by the CCL were ever returned for re-calibration. This indicates that many CO measurements are tied to the CCL through standards that may not be assessed for stability and that the scale implementation at the lab may not be tracking the changes in the scale observed at the CCL. This makes blanket corrections for atmospheric data difficult.

We recognize that not all atmospheric measurement records can be reprocessed reliably and that some measurement programs may not need the highest measurement data quality to meet program goals. Due to the time dependence of the X2014A to X2025 revision, it is not possible for the CCL to provide a single scale conversion function that would be applicable to atmospheric data from all labs. Conversion functions would be related to when the lab had standards calibrated by the CCL rather than the date the atmospheric measurements were made.

The changes in the scale from 2004 to 2020 (see Figure 9) are very small relative to typical atmospheric CO signals. Differences going back in time from 2004 do increase but are still small considering the size of signals in the atmosphere and the quality of the measurement techniques generally available to monitoring programs at that time. Scale differences since 2020 have become significant for background monitoring applications, especially for programs using low mole fraction standards (see Figure 10). However, the scale difference at higher mole fractions are less. Therefore, we think it is appropriate to consider the two scales functionally equivalent in cases where the GGMT recommended extended network compatibility goal (WMO 2026) is the relevant data quality objective. We would expect biases due to the scale differences to remain below 5 ppb in most cases where the tie to the scale was made prior to ~2023.

In cases where the more stringent GGMT network compatibility goals are required but data reprocessing is not possible, data providers will need to examine their tie to the CCL in detail to decide on appropriate atmospheric data conversion methods and related uncertainties. The CCL can help in these cases if the traceability path is well documented. In the supplemental, we

include linear fits to the X2025 vs X2014A scales. These are binned in 2 year intervals to approximate the slow mole fraction dependent change in X2014A. These, or a similar analysis of other time periods, may be useful in cases where the tie to the scale is documented but the data cannot be reprocessed.

9. CO stability in aluminum standards

The problem of growth of CO in aluminum cylinders has been recognized for many years. This has significantly complicated the maintenance and dissemination of the WMO CO scale over the years. The CCL has methods in place to improve the stability of the scale implementation going forward by conducting regular (approximately yearly) internal tracer measurements of the primary standards. However, drift in tertiary standards disseminated to the community will continue to be a problem for labs engaged in monitoring activities. The consistency of the X2025 scale revision since 2011 allows us to provide some information on typical behaviors of tertiary standards and recommendations on biases that may develop in atmospheric measurements due to CO drift in standards.

We assessed the stability of 207 aluminum AL150 sized cylinders measured at least 10 times since 2012 within the mole fraction range 25-500 ppb. 38% of cylinders had no detectable drift within our measurement uncertainty, 61% had positive drift, 7% were identified as having a non-linear rate of change, and no cylinders were identified as having negative drift. Drift rates ranged from 0 to 2.7 ppb/year with a mean of 0.4 (\pm 0.6) ppb. (Figure 12). This potential growth of CO should be included in the uncertainty budget where working standards are not recalibrated. The GGMT recommended recalibration interval for CO standards is 3 years which seems appropriate for most applications.

The cause of different CO growth rates and decelerating growth rates over time is not known. However, the potential for non-linear growth of CO in cylinders needs to be recognized and it should be considered as a potential source of error in measurements. The CCL will continue to evaluate cylinder behavior.

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Table 1: Analytical systems used for CO calibrations

System	Instrument_id	Manufacturer	Method	In service	Calibration strategy	Calibration range
RGD2	R2	Trace Analytical	GC-HGO	1988 - 1997	Multi-point calibration curve	50-200
	R7	Trace Analytical	GC-HGO	1997-2006	Multi-point calibration curve	50-200; 25-~500 after 2000
cocal-1	V1	AeroLaser	VURF	2004-2009	Single standard with zero	0 - 400 ppb
Magicc-2	V2	AeroLaser	VURF	2010	Single standard with zero (CA07318 moved from V1 to V2 after V1 failure)	0- 400 ppb
cocal-1	LGR2	Los Gatos Research	OA-ICOS	2011-2021	Multi-point calibration curve	25-500, expanded to 1000 in 2014
	V3	AeroLaser	VURF	2015-2023	Multi-point calibration curve	25-1000
	V2	AeroLaser	VURF	2023-2024	Multi-point calibration curve	25-1000
	V3	AeroLaser	VURF	2024-2025	Multi-point calibration curve	25-1000
	AR3	Aerodyne	QC-TILDAS	2022-	Multi-point calibration curve	25-1000

Figure 1: CO Gravimetric tree. Colors indicate groups of standards. White boxes indicate gravimetric standards that were not used to define the scale with the exception of 2006 grav CA04503 which should have been color coded green as it is included.

CO gravimetric standards, updated Nov. 2015

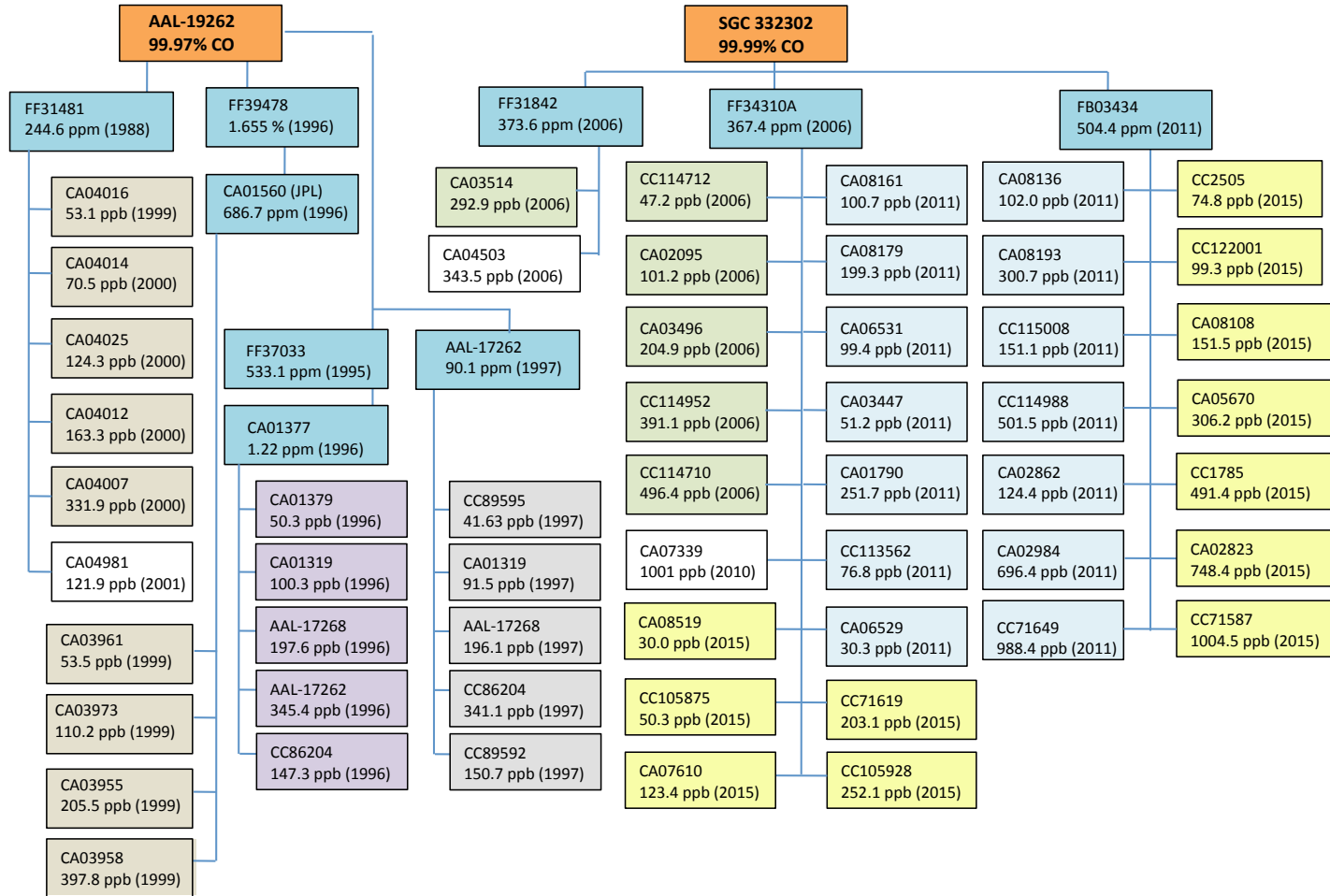


Table 2: 2011 primary standards. Date of production and gravimetrically determined values are shown.

# 2011 Primary CO standards			
serial_number	date	gravimetric value	gravimetric unc
CA06529	2011-12-07	30.32	0.18
CA03447	2011-11-02	51.21	0.22
CC113562	2011-11-30	76.57	0.28
CA06531	2011-11-02	99.37	0.33
CA08161	2011-08-20	100.69	0.34
CA08136	2011-09-15	102.10	0.32
CA02862	2011-12-08	124.35	0.39
CC115008	2011-11-15	151.12	0.45
CA08179	2011-08-22	199.32	0.59
CA01790	2011-11-15	251.68	0.74
CA08193	2011-09-15	300.65	0.85
CC114988	2011-11-30	501.48	1.41
FB03434	2011-07-21	504.44	1.36
CA02984	2011-12-16	696.37	1.96
CC71649	2011-12-28	988.42	3.97

Table 3: Parent tanks for bootstrap standards. Values and uncertainties derived from gravimetric production of each parent tank.

Id	CO (unc)	CH ₄ (unc)	CO:CH ₄ ratio (unc)
FB03858	0.001674 (0.000002)	0.037710 (0.000022)	0.0444 (0.0006)
FB03863	0.008763 (0.000002)	0.028798 (0.000007)	0.3043 (0.0001)
FB03885	0.003452 (0.000002)	0.032606 (0.000005)	0.1059 (0.0001)

Table 4: Table of dilution standards from the August 2015 calibration episode. Uncertainties include the gravimetric uncertainty of the parent mixtures, CO and CH₄ in the diluent air, and ability to measure the CH₄ mole fraction of each dilution standard.

ID	Parent	Diluent	[CH ₄] _z	[CO] _z	[CH ₄] _m (unc)	[CO] _{assigned} (unc)
FF32810	FB03858	CB10223	4.5	0.0	557.6 (1.6)	24.6 (0.2)
FF32779	FB03858	CB10223	4.5	0.0	1082.5 (1.1)	47.9 (0.2)
FB04080	FB03885	CB09903	4.5	0.0	551.1 (1.7)	57.9 (0.3)
FB03876	FB03858	CB10223	4.5	0.0	1759.5 (1.8)	77.9 (0.2)
FB04083	FB03885	CB09903	4.5	0.0	775.6 (1.6)	81.6 (0.3)
FB03856	FB03858	CB10223	4.5	0.0	2204.2 (2.2)	97.7 (0.3)
FB03884	FB03858	CB10223	4.5	0.0	2829.6 (2.8)	125.4 (0.3)
FB04095	FB03885	CB10223	4.5	0.0	1189.1 (1.2)	125.4 (0.2)
FB03850	FB03863	CB09903	4.5	0.0	481.7 (1.4)	145.2 (0.6)
FB03861	FB03858	CB10223	4.5	0.0	3433.9 (3.4)	152.2 (0.3)
FB04096	FB03885	CB10223	4.5	0.0	1786.0 (1.8)	188.6 (0.3)
FB03852	FB03863	CB09903	4.5	0.0	794.0 (1.6)	240.2 (0.6)
FB03851	FB03863	CB09903	4.5	0.0	1101.5 (1.1)	333.8 (0.5)
FB03869	FB03863	CB09903	4.5	0.0	1737.6 (1.7)	527.4 (0.7)
FB03888	FB03863	CB09903	4.5	0.0	2450.2 (2.5)	744.2 (0.9)
FB04059	FB03863	CB09903	4.5	0.0	3505.0 (3.5)	1065.3 (1.2)

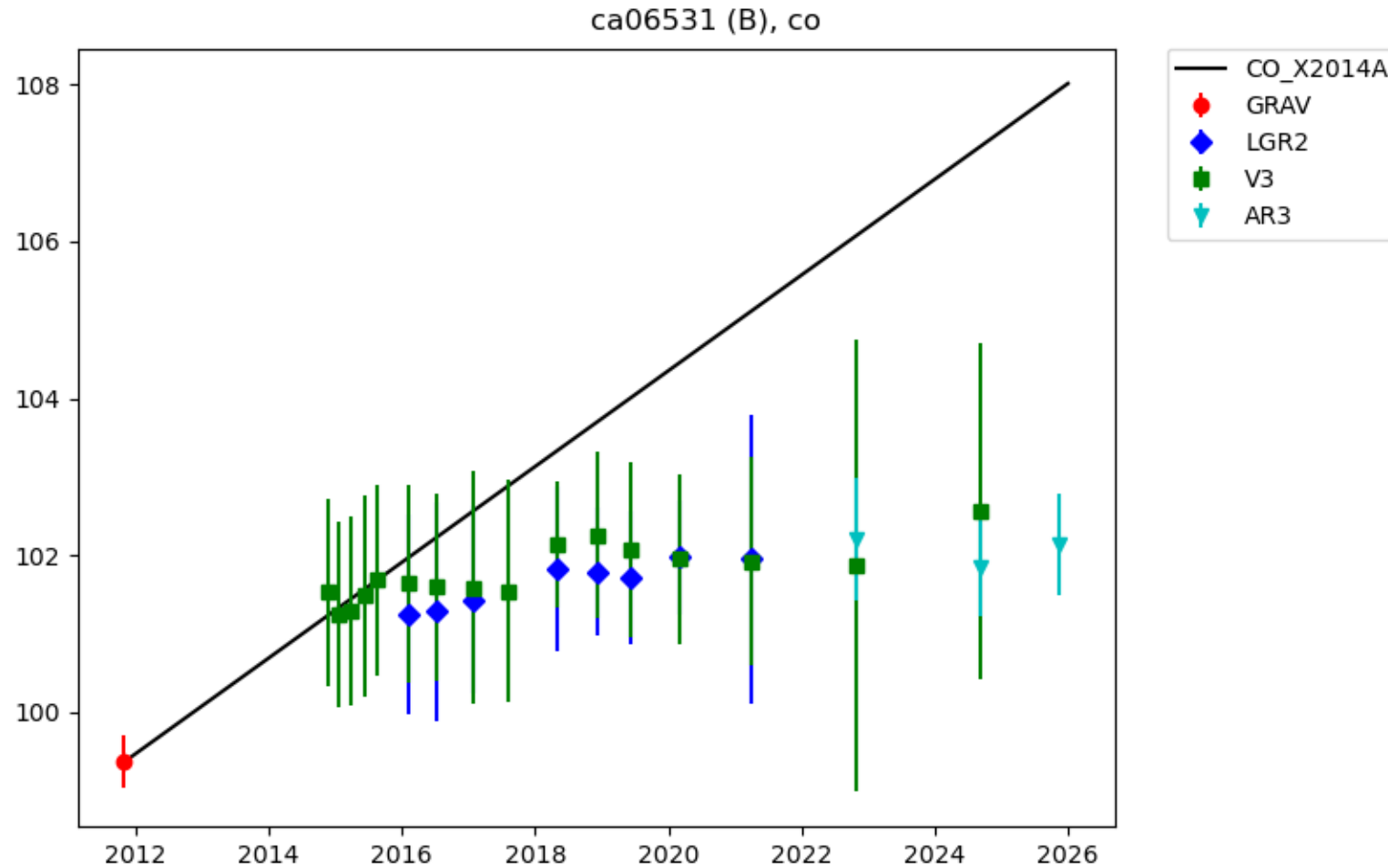


Figure 2. Gravimetric value and calibration history of primary standard CA06531, one of the 14 2011 primary standards. CA06531 was made gravimetrically in 2011, with the gravimetric determined value shown in red. It has been measured 1-2 times per year against standards produced using the internal tracer technique on various instruments (LGR2, V3, AR3) since 2014. Black line shows the time dependent value assignment used to define the X2014A scale. The difference between the measurement results and the line indicates a growing positive bias in this 2011 primary standard.

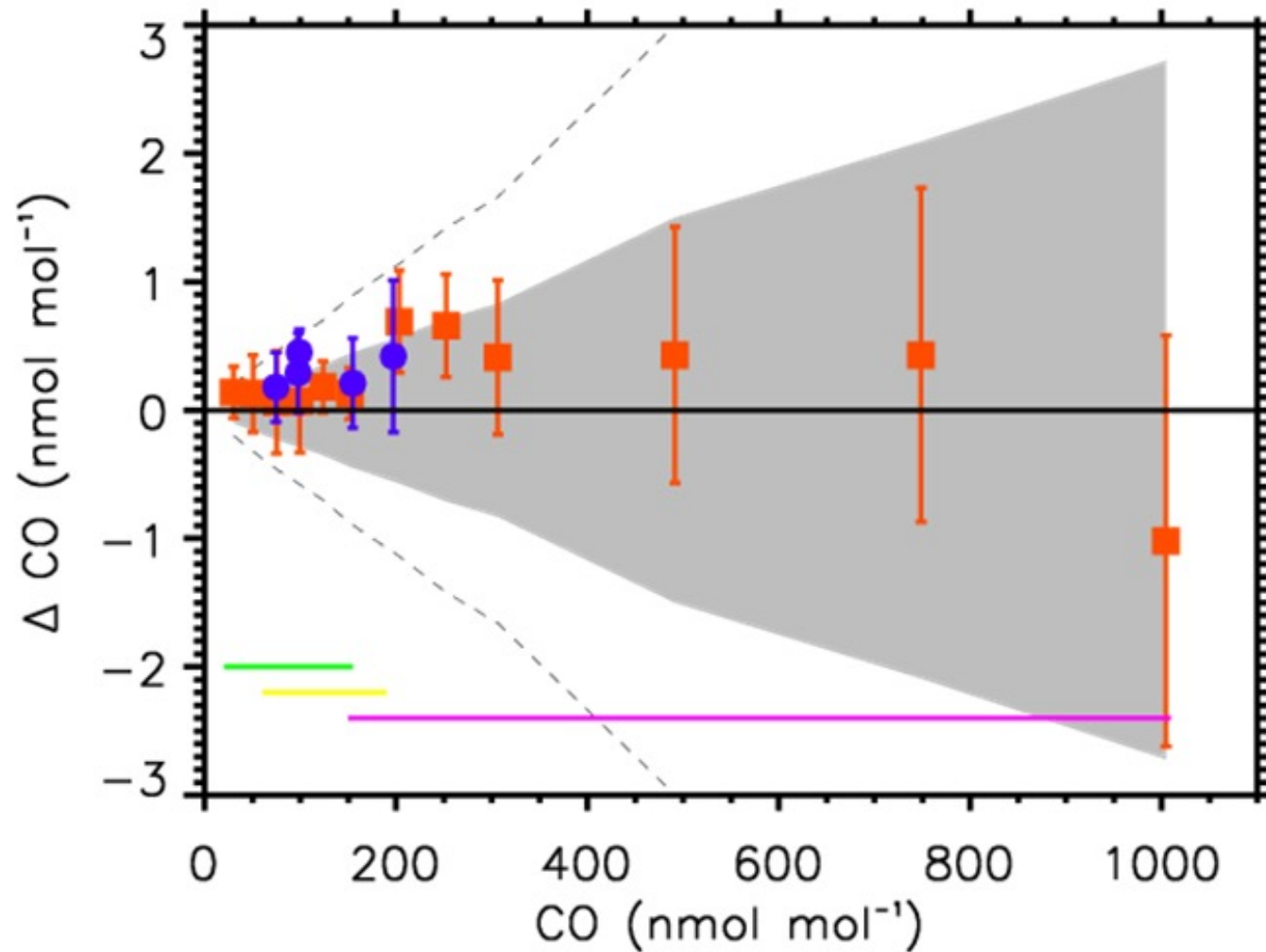


Figure 3: Results of the 2015 and 2017 gravimetric standards measured vs standards made using the internal tracer method. Measurements were made within two weeks of the gravimetric production dates. Colored bars represent the CO mole fraction range covered by each of the three parent mixtures.

Figure 4 - History of 2015 gravimetric standard CA07610 with an imposed 2 year data gap (shown by open symbols as not being included in the fit).

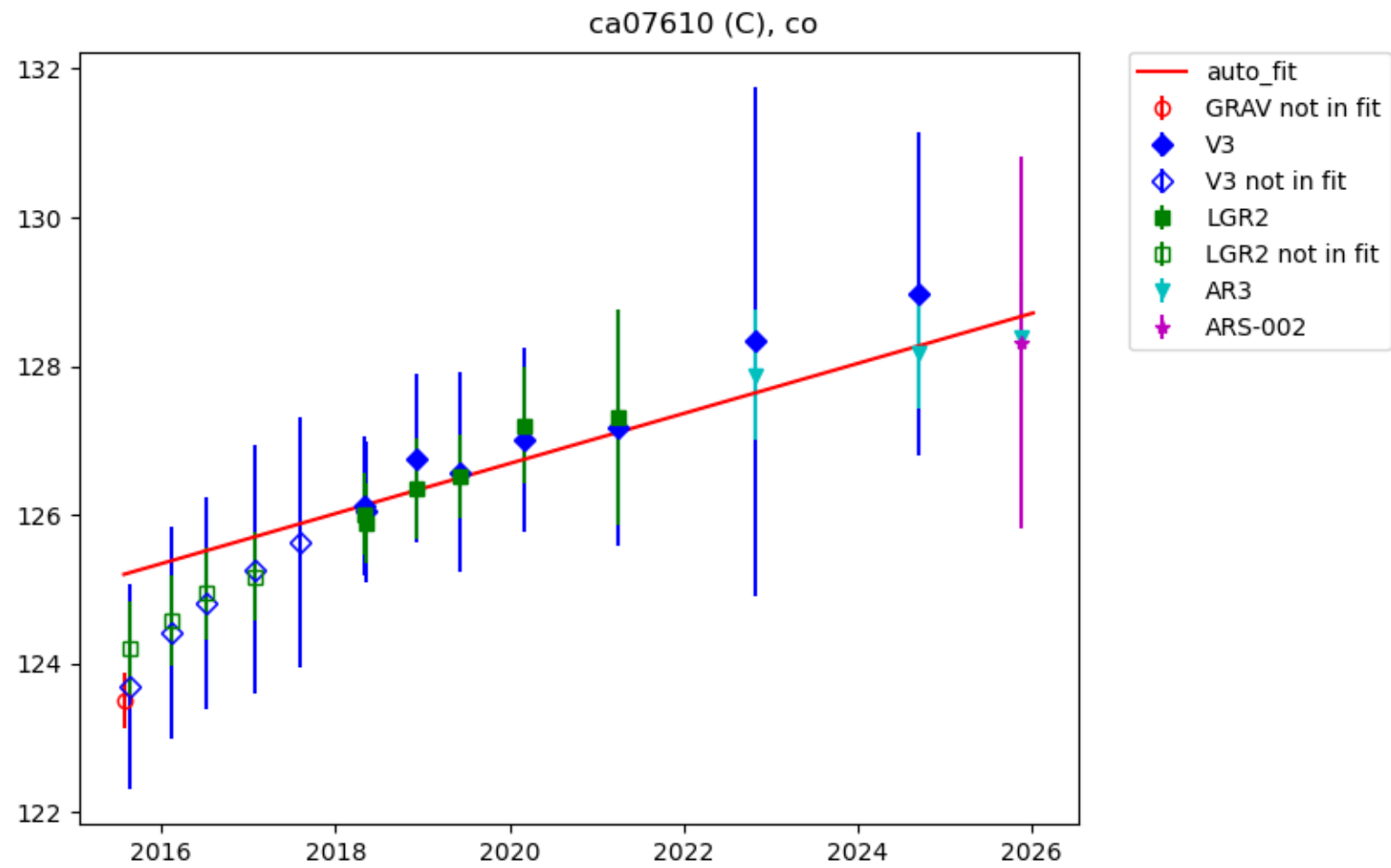


Figure 5: X2025 value assignments (both fits) for 2011 primary standard CA08161. Vertical dashed line indicates transition point from first to second value assignment in June 2016.

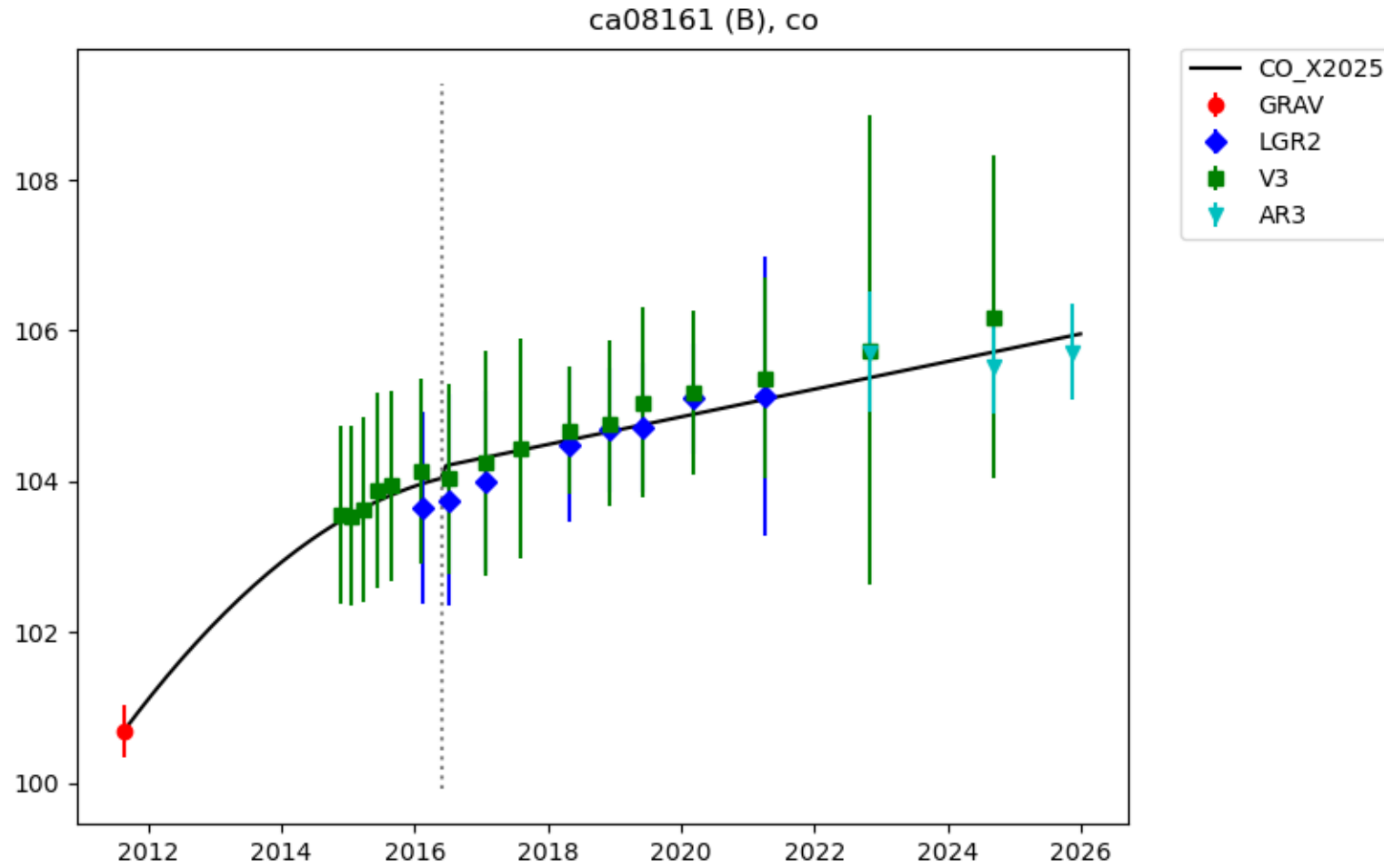


Table 5 - X2025 Value assignments for 2011 primary standards

serial_num	fillcode	start_date	tzero	coef0	coef1	coef2	comment
CA06529	C	2011-12-07	2013.210150	31.062295	0.517118	-0.049232	"first of 2 split fits use quad fit to grav plus dilution measurements through end of 2017"
CA06529	C	2016-06-01	2020.328450	32.544820	0.000000	0.000000	"second of 2 split fits use fit to dilution measurements through 2025 only"
CA03447	B	2011-11-02	2013.281633	51.822976	0.364462	-0.041218	"first of 2 split fits use quad fit to grav plus dilution measurements through end of 2017"
CA03447	B	2016-06-01	2020.639037	52.977355	0.000000	0.000000	"second of 2 split fits use fit to dilution measurements through 2025 only"
CC113562	B	2011-11-30	2013.614695	77.314504	0.367536	-0.041073	"first of 2 split fits use quad fit to grav plus dilution measurements through end of 2017"
CC113562	B	2016-06-01	2020.766370	78.616398	0.000000	0.000000	"second of 2 split fits use fit to dilution measurements through 2025 only"
CA06531	B	2011-11-02	2013.738710	100.803422	0.554650	-0.103886	"first of 2 split fits use quad fit to grav plus dilution measurements through end of 2017"
CA06531	B	2016-06-01	2020.539234	101.893337	0.000000	0.000000	"second of 2 split fits use fit to dilution measurements through 2025 only"
CA08161	B	2011-08-20	2013.651213	102.671484	0.776395	-0.101290	"first of 2 split fits use quad fit to grav plus dilution measurements through end of 2017"
CA08136	B	2011-09-15	2013.551861	104.394937	1.032541	-0.112481	"first of 2 split fits use quad fit to grav plus dilution measurements through end of 2017"
CA08161	B	2016-06-01	2020.571053	104.960270	0.183297	0.000000	"second of 2 split fits use fit to dilution measurements through 2025 only"
CA08136	B	2016-06-01	2020.414934	107.665532	0.273305	0.000000	"second of 2 split fits use fit to dilution measurements through 2025 only"
CA02862	B	2011-12-08	2013.913120	124.945390	0.224414	-0.038750	"first of 2 split fits use quad fit to grav plus dilution measurements through end of 2017"
CA02862	B	2016-06-01	2020.409410	125.453610	0.000000	0.000000	"second of 2 split fits use fit to dilution measurements through 2025 only"
CC115008	C	2011-11-14	2013.954410	152.554111	0.578440	-0.051898	"first of 2 split fits use quad fit to grav plus dilution measurements through end of 2017"
CC115008	C	2016-06-01	2020.282663	154.649404	0.000000	0.000000	"second of 2 split fits use fit to dilution measurements through 2025 only"
CA08179	B	2011-08-22	2014.116052	201.275793	0.598538	-0.076357	"first of 2 split fits use quad fit to grav plus dilution measurements through end of 2017"
CA08179	B	2016-06-01	2020.114850	203.100869	0.000000	0.000000	"second of 2 split fits use fit to dilution measurements through 2025 only"
CA01790	C	2011-11-15	2014.555735	252.252553	0.212462	0.000000	"first of 2 split fits use linear fit to grav plus dilution measurements through end of 2017"
CA01790	C	2016-06-01	2019.800140	253.096373	0.000000	0.000000	"second of 2 split fits use fit to dilution measurements through 2025 only"
CA08193	B	2011-09-15	2014.374813	302.187017	0.563815	0.000000	"first of 2 split fits use linear fit to grav plus dilution measurements through end of 2017"
CA08193	B	2016-06-01	2019.920550	304.210025	0.000000	0.000000	"second of 2 split fits use fit to dilution measurements through 2025 only"
CC114988	C	2011-11-30	2014.726315	503.194252	0.642781	0.000000	"first of 2 split fits use linear fit to grav plus dilution measurements through end of 2017"
CC114988	C	2016-06-01	2019.778769	505.197781	0.000000	0.000000	"second of 2 split fits use fit to dilution measurements through 2025 only"
CA02984	B	2011-12-16	2014.795504	697.399861	0.000000	0.000000	"first of 2 split fits use mean of grav plus dilution measurements through end of 2017"
CA02984	B	2016-06-01	2019.785278	698.664352	0.000000	0.000000	"second of 2 split fits use fit to dilution measurements through 2025 only"
CC71649	F	2011-12-28	2015.425605	990.517340	0.000000	0.000000	"first of 2 split fits use mean of grav plus dilution measurements through end of 2017"
CC71649	F	2016-06-01	2019.749910	993.436176	0.000000	0.000000	"second of 2 split fits use fit to dilution measurements through 2025 only"

Table 6 - X2025 Value assignments for current secondary standards

serial_num	fillcode	start_date	tzero	coef0	coef1	coef2	comment
ND46739	A	2011-01-01	2013.821799	24.515336	0.503840	0.000000	"first of 2 split fits assigned by official cal results 2011-2017"
ND46739	A	2016-06-01	2020.265535	25.969202	0.070967	0.000000	"second of 2 split fits assigned by linear fit to official cal results 2014-2025"
ND39723	A	2010-01-01	2013.828480	44.751477	0.540345	0.000000	"first of 2 split fits. assigned by official cal results 2011-2017"
ND39723	A	2016-06-01	2020.321071	46.603303	0.139578	0.000000	"second of 2 split fits. assigned by official cal results 2014-2025"
ND39910	A	2010-01-01	2013.839292	84.493229	0.765133	0.000000	"first of 2 split fits. assigned by official cal results 2011-2017"
ND39910	A	2016-06-01	2020.345506	87.378429	0.209269	0.000000	"second of 2 split fits. assigned by official cal results 2014-2025"
ND39908	A	2010-01-01	2013.847323	125.545406	0.500567	0.000000	"first of 2 split fits. assigned by official cal results 2011-2017"
ND39908	A	2016-06-01	2020.059714	127.470615	0.000000	0.000000	"second of 2 split fits. assigned by official cal results 2014-2025"
ND39900	A	2010-01-01	2013.838087	168.162324	0.511115	0.000000	"first of 2 split fits. assigned by official cal results 2011-2017"
ND39900	A	2016-06-01	2020.012857	170.231217	0.000000	0.000000	"second of 2 split fits. assigned by official cal results 2014-2025"
ND39376	A	2010-01-01	2013.837122	208.646746	0.570331	0.000000	"first of 2 split fits. assigned by official cal results 2011-2017"
ND39376	A	2016-06-01	2019.994018	210.921820	0.000000	0.000000	"second of 2 split fits. assigned by official cal results 2014-2025"
ND39134	A	2010-01-01	2013.835158	266.900638	0.486513	0.000000	"first of 2 split fits. assigned by official cal results 2011-2017"
ND39134	A	2016-06-01	2019.994426	268.795438	0.000000	0.000000	"second of 2 split fits. assigned by official cal results 2014-2025"
ND39901	A	2010-01-01	2015.686706	359.841700	0.371197	0.000000	"assigned by official cal results 2011-2025"
ND39375	A	2010-01-01	2015.556200	517.862456	0.318027	0.000000	"assigned by official cal results 2011-2025"
ND39902	A	2010-01-01	2017.431587	754.535583	0.000000	0.000000	"assigned by official cal results 2011-2025"
ND39907	A	2010-01-01	2017.600827	992.313175	0.000000	0.000000	"assigned by official cal results 2011-2025"

Table 7 – 1999/2000 gravimetric standard value assignments.

serial_num	fillcode	start_date	tzero	coef0	coef1	coef2	comment
CA03961	A	1999-09-02	2017.512179	59.158984	0.099187	-0.010117	"Grav value plus measurements vs dilution standards and Use V1 measurement vs CA03958"
CA04016	A	1999-12-30	2013.949164	63.258061	0.247785	-0.025153	"Grav value plus measurements vs dilution standards and Use V1 measurement vs CA03958"
CA04014	A	2000-02-11	2015.915737	80.700116	0.156892	-0.025262	"Grav value plus measurements vs dilution standards and Use V1 measurement vs CA03958"
CA03973	A	1999-09-02	2016.110508	125.198075	0.305201	-0.028862	"Grav value plus measurements vs dilution standards and Use V1 measurement vs CA03958 "
CA04025	B	2000-02-11	2014.265316	130.745518	0.213474	-0.016029	"Grav value plus measurements vs dilution standards and Use V1 measurement vs CA03958"
CA04012	A	2000-02-11	2014.340009	175.820024	0.301175	-0.036227	"Grav value plus measurements vs dilution standards and Use V1 measurement vs CA03958"
CA03955	A	1999-09-03	2013.731255	208.550698	0.078656	0.000000	"Grav value plus measurements vs dilution standards and Use V1 measurement vs CA03958"
CA04007	A	2000-02-11	2012.722270	343.170269	0.452190	-0.036539	"Grav value plus measurements vs dilution standards and Use V1 measurement vs CA03958"
CA03958	A	1999-08-30	2014.378356	400.918731	0.130255	0.000000	"Grav value plus measurements vs dilution standards and 2015 gravs"

Figure 6 – Value assignment of CA03958. The nearly stable 1999/2000 gravimetric standard used to calibrate the other members of that set.

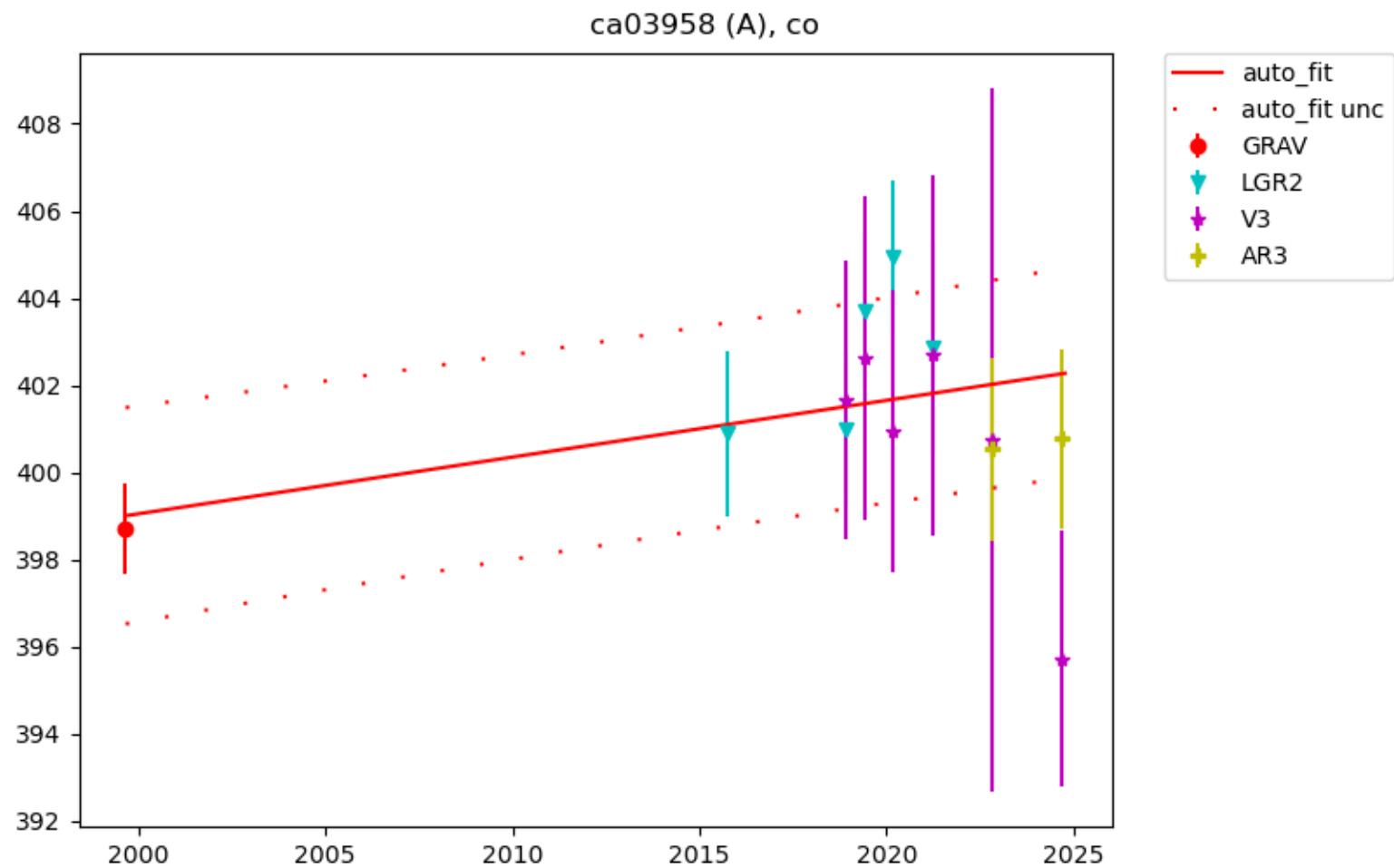


Figure 7 – example of one of the 1999/2000 gravimetric standards (CA03973) with calibrations vs CA03958 on instrument V1 included.

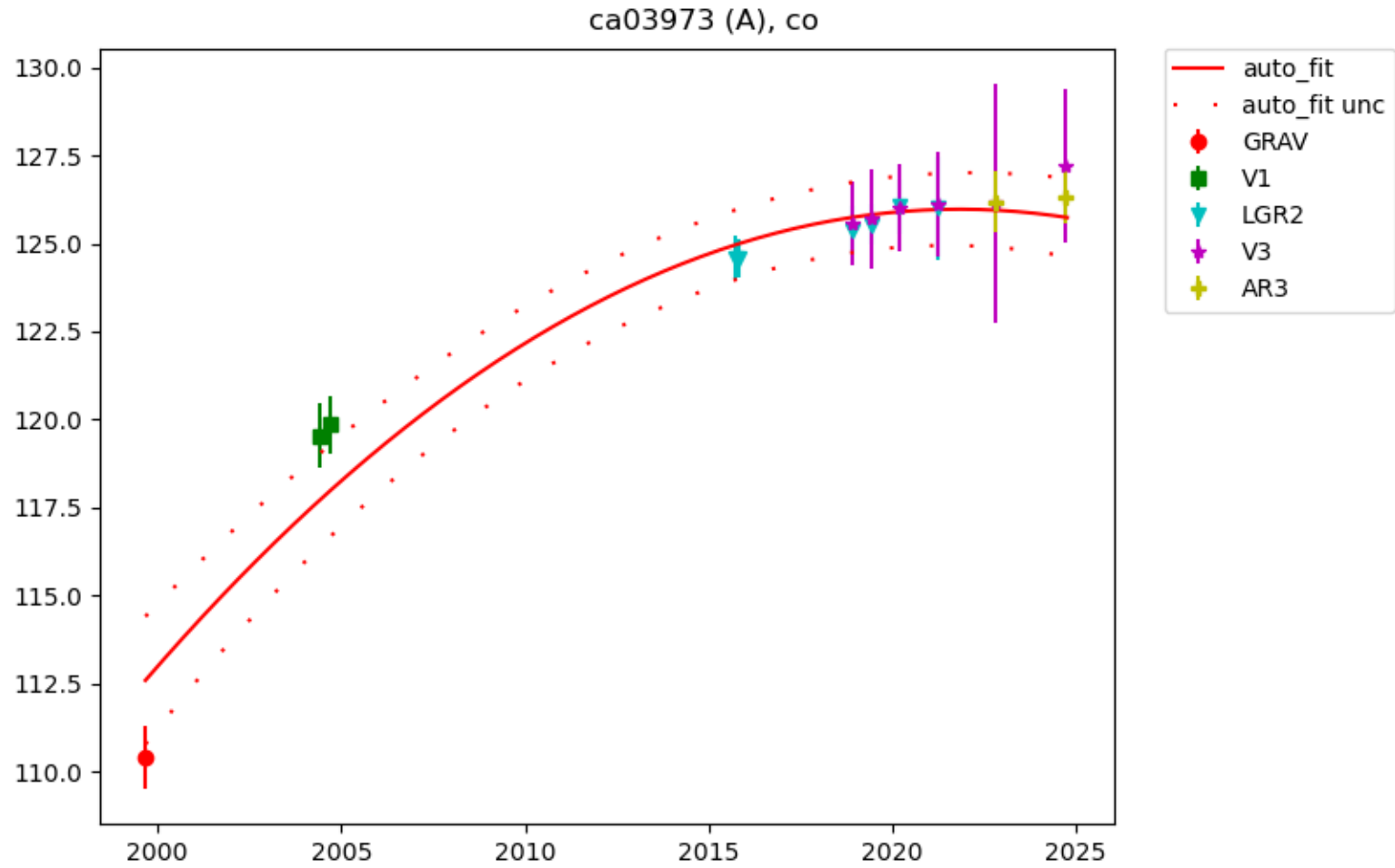


Figure 8 - plot ca07318 including measurements against current secondary standards which are not included in the value assignment fit. (use `-plot_flag=s,S` in caldrift call) While not included in the fit, these measurements vs the secondary standards do help justify the assumption of a linear drift between 2007 and the more recent measurements.

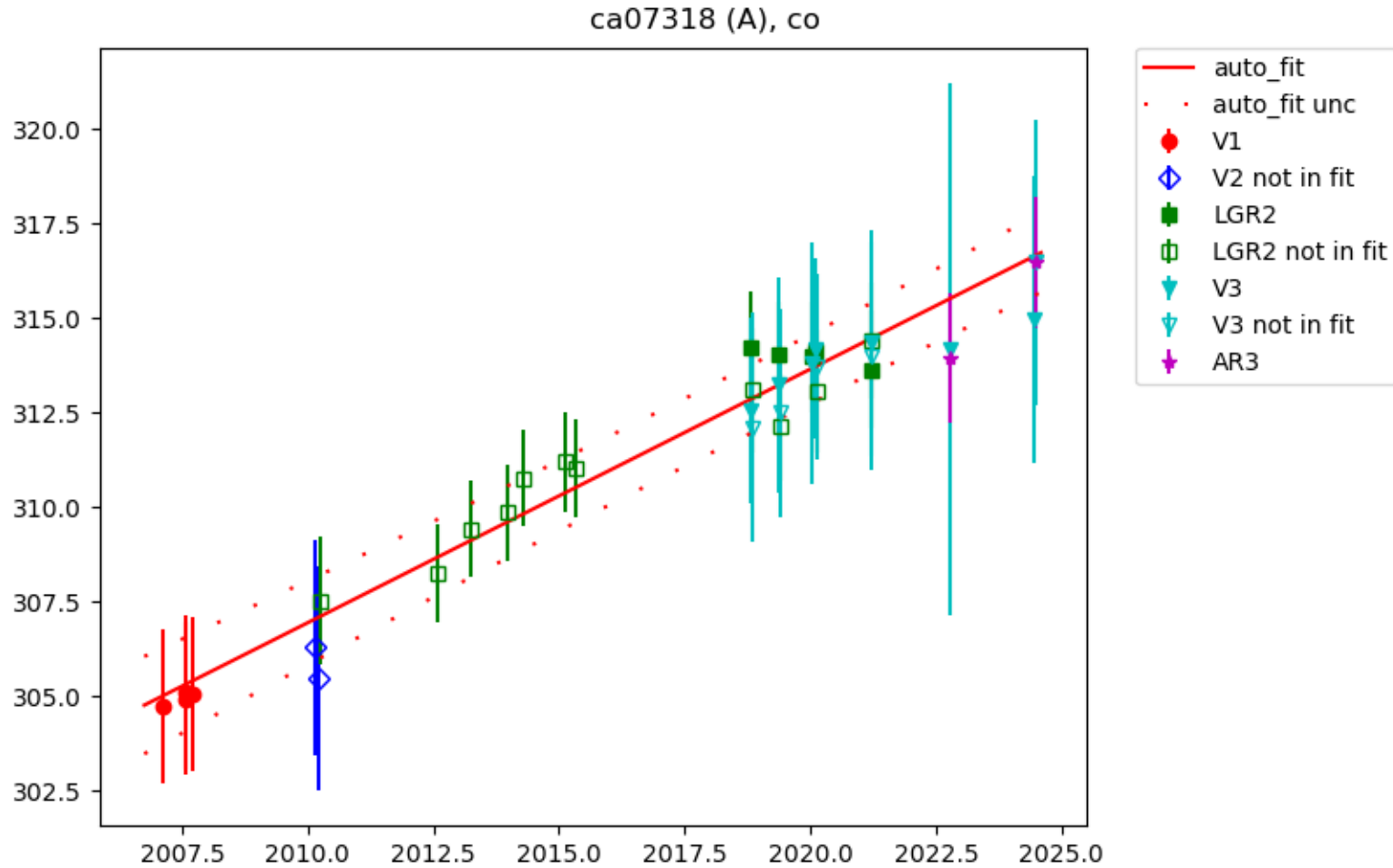


Table 8 – Long term target tanks used from March 2010 – April 2011 as standards on the cocal-1 system. Values are as of April 2011 on CO_X2025 scale. Value assignments for these cylinders are derived only from measurements against the 2011 primary standards. (use `-include_flag=S` in caldrift call)

S1	ND33962	24.9	(+- 0.6)
S2	ND15749	58.3	(+- 0.5)
S3	ND17445	107.4	(+- 0.5)
S4	ND17435	153.8	(+-0.6)
S5	ND17431	203.6	(+-0.7)
S6	ND16416	304.5	(+-1.1)

Table 9 – Standards used on the RGD2 system 1993-1999

serial_num	fillcode	start_date	tzero	coef0	coef1	coef2	comment
CC68734	A	1989-02-01	2018.243242	175.076512	0.362091	0.000000	"RGD2 secondary"
CC73110	A	1990-01-15	2012.173981	206.086085	0.090907	0.000000	"RGD2 secondary"
CC71607	A	1991-10-01	2014.695726	142.458661	0.124709	0.000000	"RGD2 secondary"
CC114712	A	1992-01-01	2003.371719	63.653481	0.888800	0.000000	"RGD2 secondary"
CC105467	A	1992-02-01	2012.853345	91.013846	0.205738	-0.012405	"RGD2 secondary"
CC104208	A	1992-03-19	2019.094551	54.262702	0.154271	0.000000	"measured vs 2015 2011 dilution standards and on r7 vs 1999 gravs. Using linear based on residuals over time for response curves"
CC105460	A	1992-03-19	1998.878529	112.112649	0.196162	-0.242263	"1992 grav. Used on rdg2 1993-2000. measured vs 1996 1997 and 1999 gravs. Using quadratic based on residuals over time for response curves"
CC86203	A	1992-03-20	1992.200000	147.199998	0.000000	0.000000	"No measurements assigned gravimetric value plus time dependent unc term of 0.5 per year"
CC114932	A	1993-01-01	2018.084756	180.140821	0.171044	0.000000	"RGD2 secondary force linear fit"
CA01493	A	1995-01-01	1999.673058	152.284791	0.000000	0.000000	"RGD2 secondary and magicc RGA std force linear fit"

Figure 9 $-X_{2025} - X_{2014A}$ for tertiary standards vs analysis date.

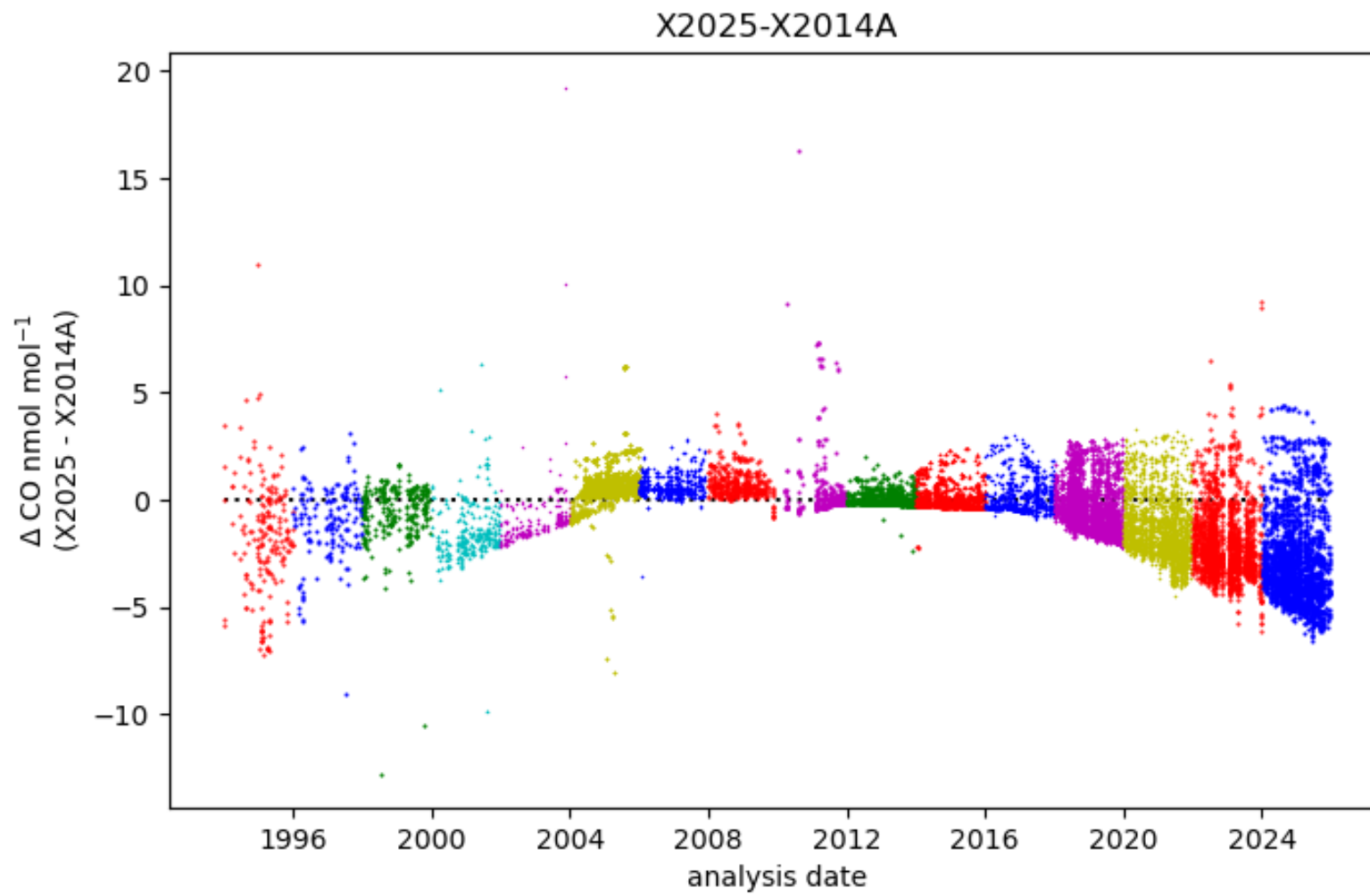


Figure 10 – X2025 – X2014A values for tertiary standards measured from 2018 – 2025 plotted versus mole fraction. The largest biases in X2014A occurred at the low end of the scale range. The bias at 50 ppb reached +5 ppb in 2025. However, biases are lower at the upper end of the scale range with biases in measurements made 2025 of 0 ppb at 500 ppb and only -2 ppb at 700 ppb.

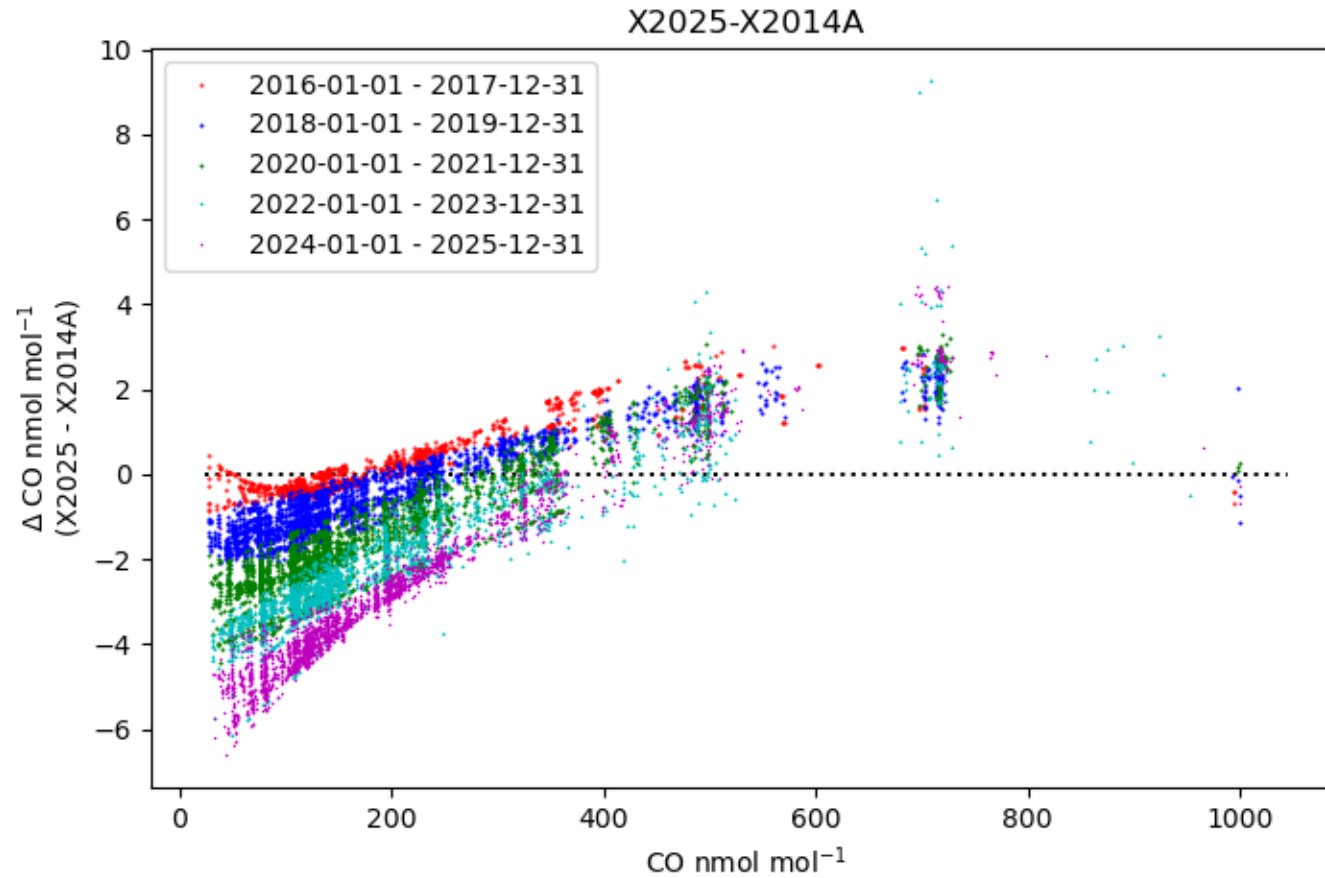


Figure 11 - Calibration histories of long-term target tanks. These tanks have been measured a few times per year since 2001. Top panel show calibration history, bottom panel are residuals to linear fit to the data.

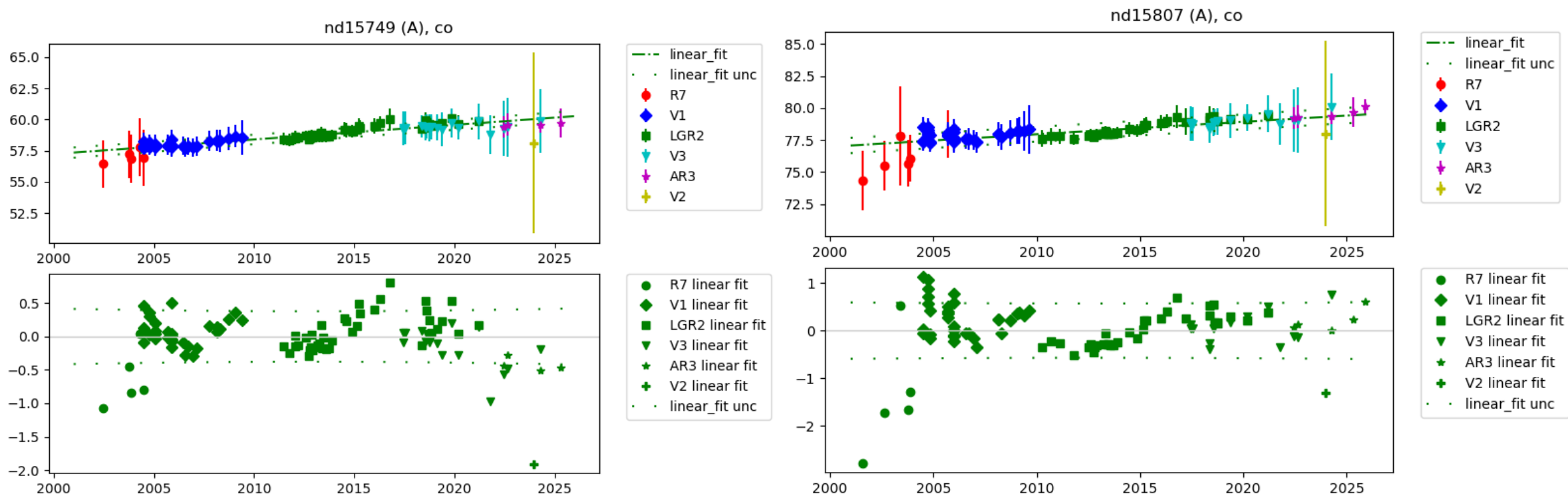


Figure 11 cont. - Calibration histories of long-term target tanks. These tanks have been measured a few times per year since 2001. Top panel show calibration history, bottom panel are residuals to linear fit to the data.

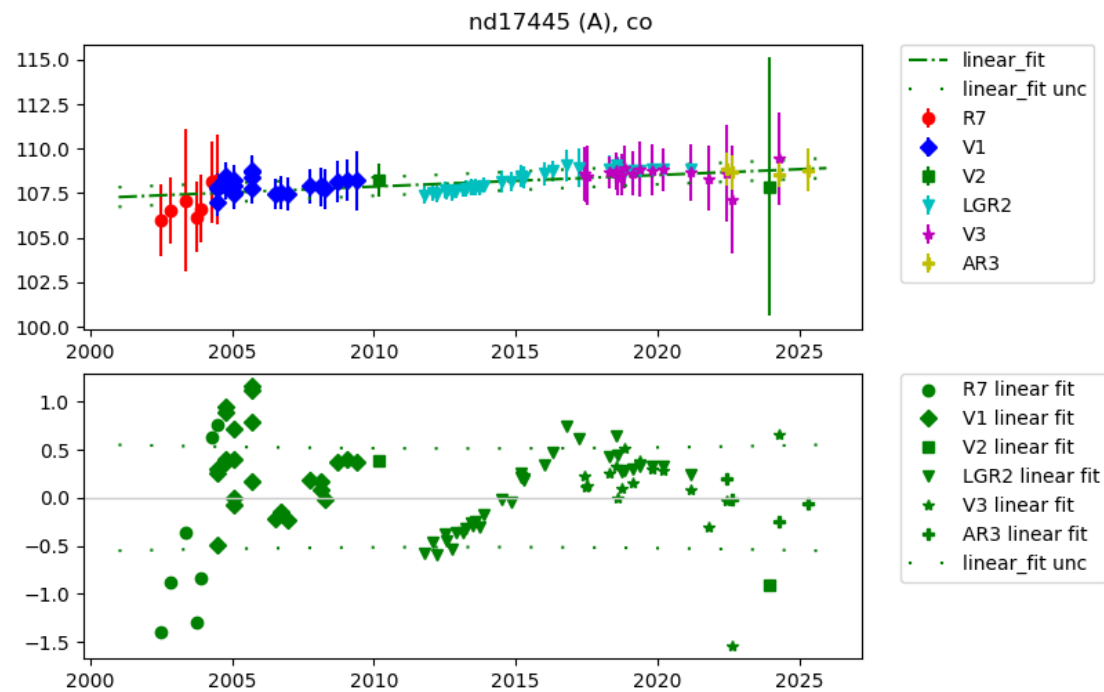
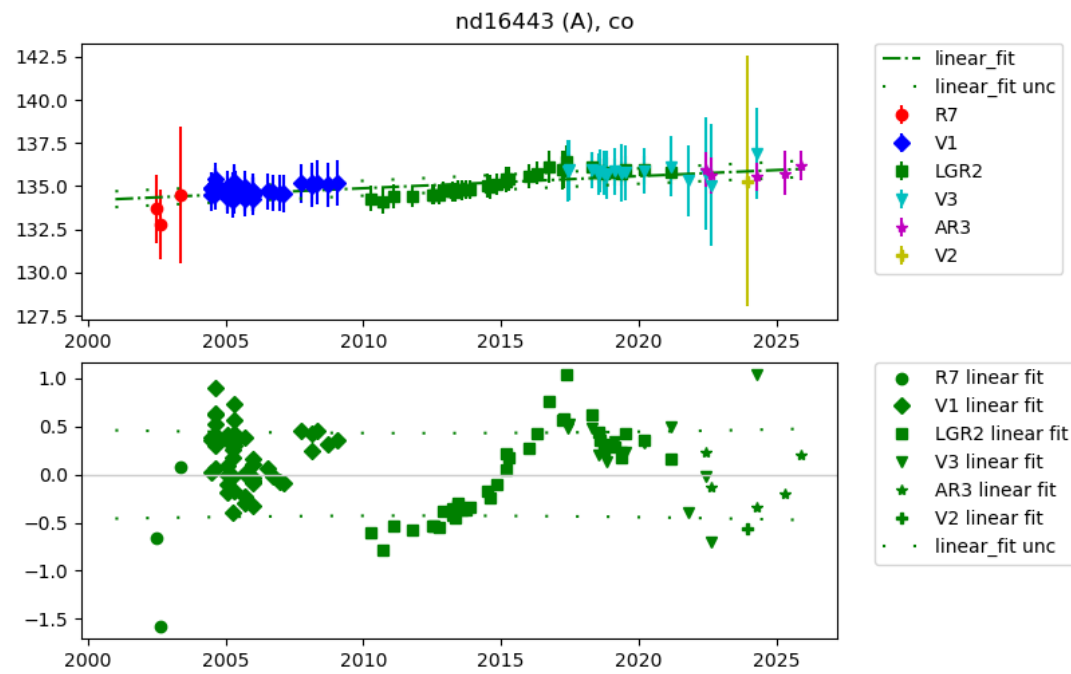
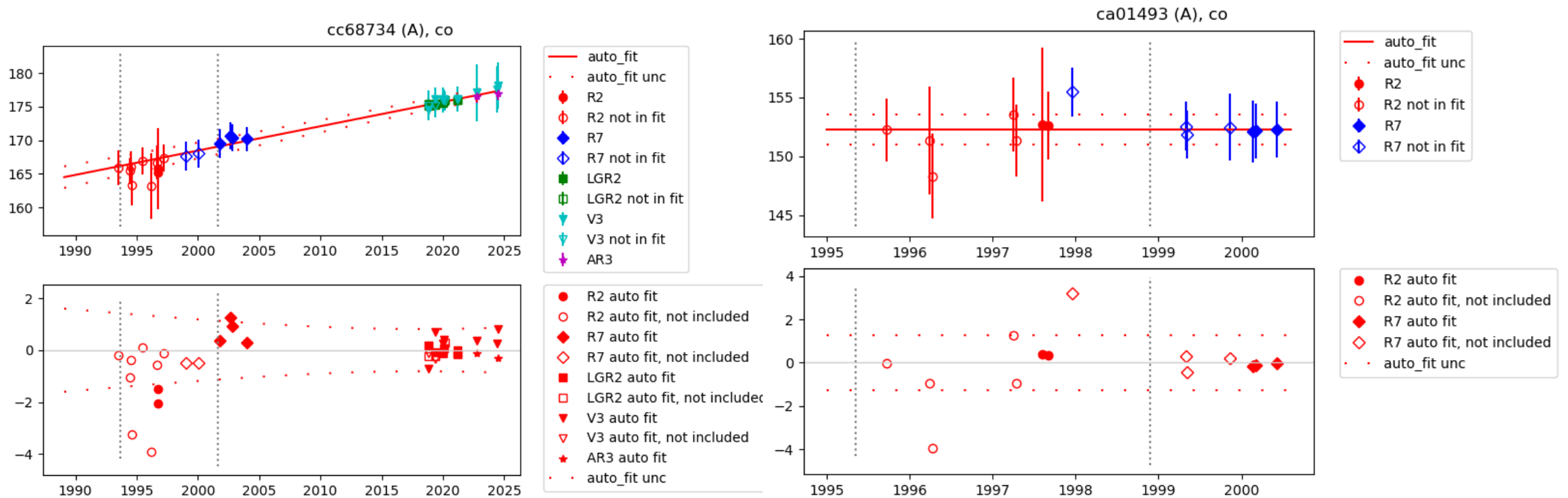


Table 10: Long term target tanks used to monitor consistency of scale transfer to tertiary standards. Linear fit to lower amount fraction tanks, mean of higher. Residuals are ~0.5 ppb below 300 ppb and less than 1% above. Lower mole fraction tanks likely have non-linear drift occurring but have used a linear fit for this analysis.

serial_num	fillc ode	fill_date	tzero	coef0	unc_c0	coef1	unc_c1	rsd	n
ND33962	A	2008-01-01	2015.84976	26.029	0.095	0.22475	0.02552	0.9	58
ND33423	A	2008-01-01	2015.54751	43.651	0.093	0.17084	0.02207	0.42	56
ND15749	A	2001-01-01	2012.80895	58.72	0.067	0.11677	0.01419	0.37	96
ND15807	A	2001-01-01	2012.7304	78.215	0.073	0.09739	0.014	0.57	93
ND17445	A	2001-01-01	2013.30088	108.086	0.079	0.06506	0.01637	0.51	89
ND16443	A	2001-01-01	2012.14689	135.028	0.082	0.07022	0.01467	0.42	112
ND17435	A	2001-01-01	2013.03	154.612	0.096	0.06495	0.01785	0.48	100
ND16439	B	2018-10-11	2021.14725	171.663	0.271	0.05456	0.11831	0.57	22
ND17431	A	2001-05-01	2012.0231	203.397	0.12	0.01282	0.02274	0.58	97
ND33961	A	2008-01-01	2016.05001	241.269	0.18	0.20202	0.04322	0.78	55
ND16416	A	2002-01-01	2013.61744	304.116	0.19	0.05579	0.03614	0.74	75
ND33960	C	2014-03-05	2018.62358	489.603	0.425	0.00000	0.00000	1.94	41
CB10910	B	2016-02-18	2019.44292	704.789	0.621	0.00000	0.00000	2.31	42
CA07339	B	2010-03-01	2018.3665	1003.756	0.967	0.00000.	0.00000	3.84	44

Figure 13 – Two examples of secondary standard used on the RGD2 system during the 1990’s. Closed symbols show results vs primary standards that are used to value assign the secondary standards. Open symbols are results against other secondary standards in use during the 1990’s. These circulate calibrations were done in an attempt to identify drifting members of the secondary set. They are not used in the value assignment but do give some indication of the consistency of the scale transfer over time. Vertical dashed lines indicate the time in service of each standard.

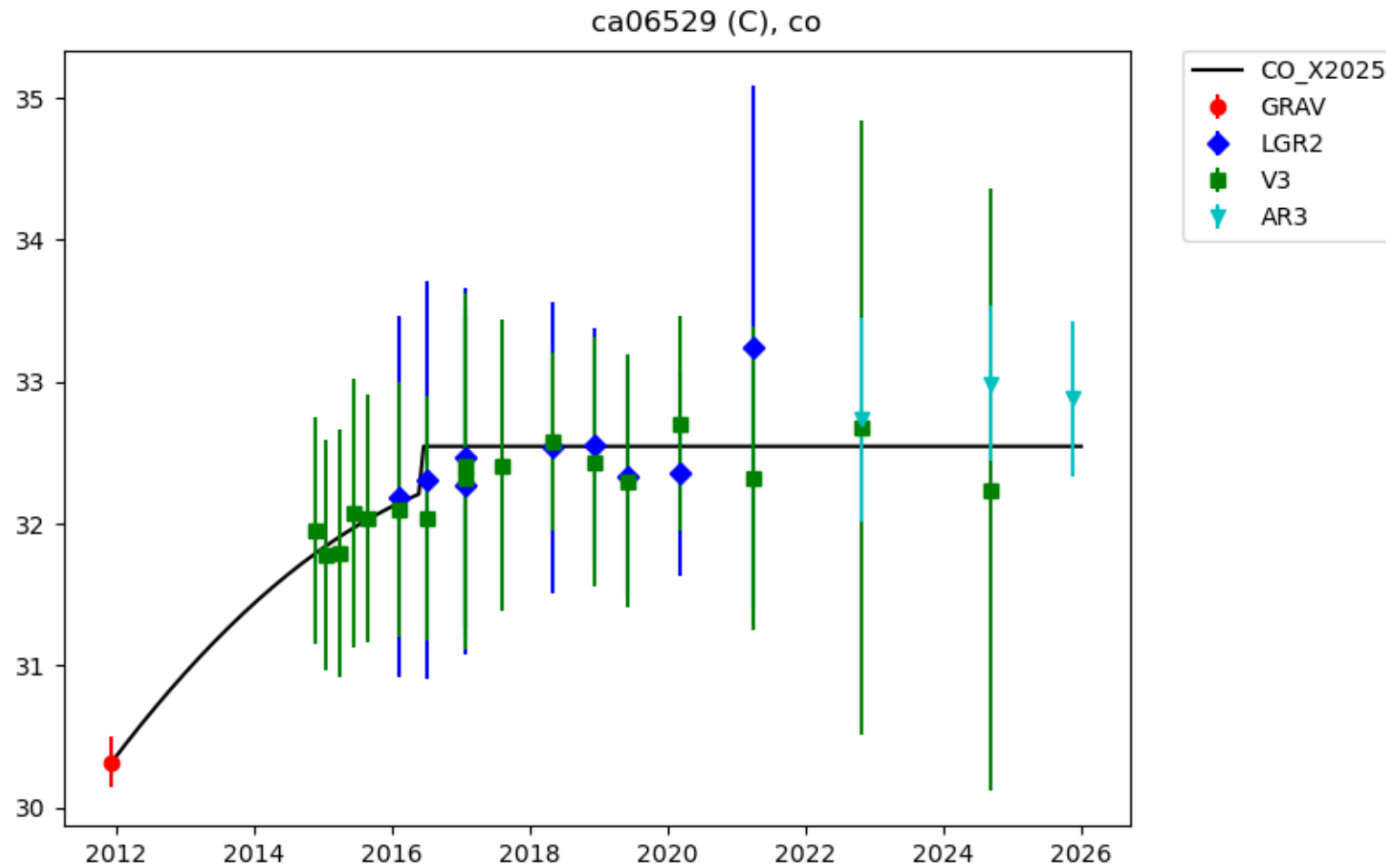


Supplemental Figures

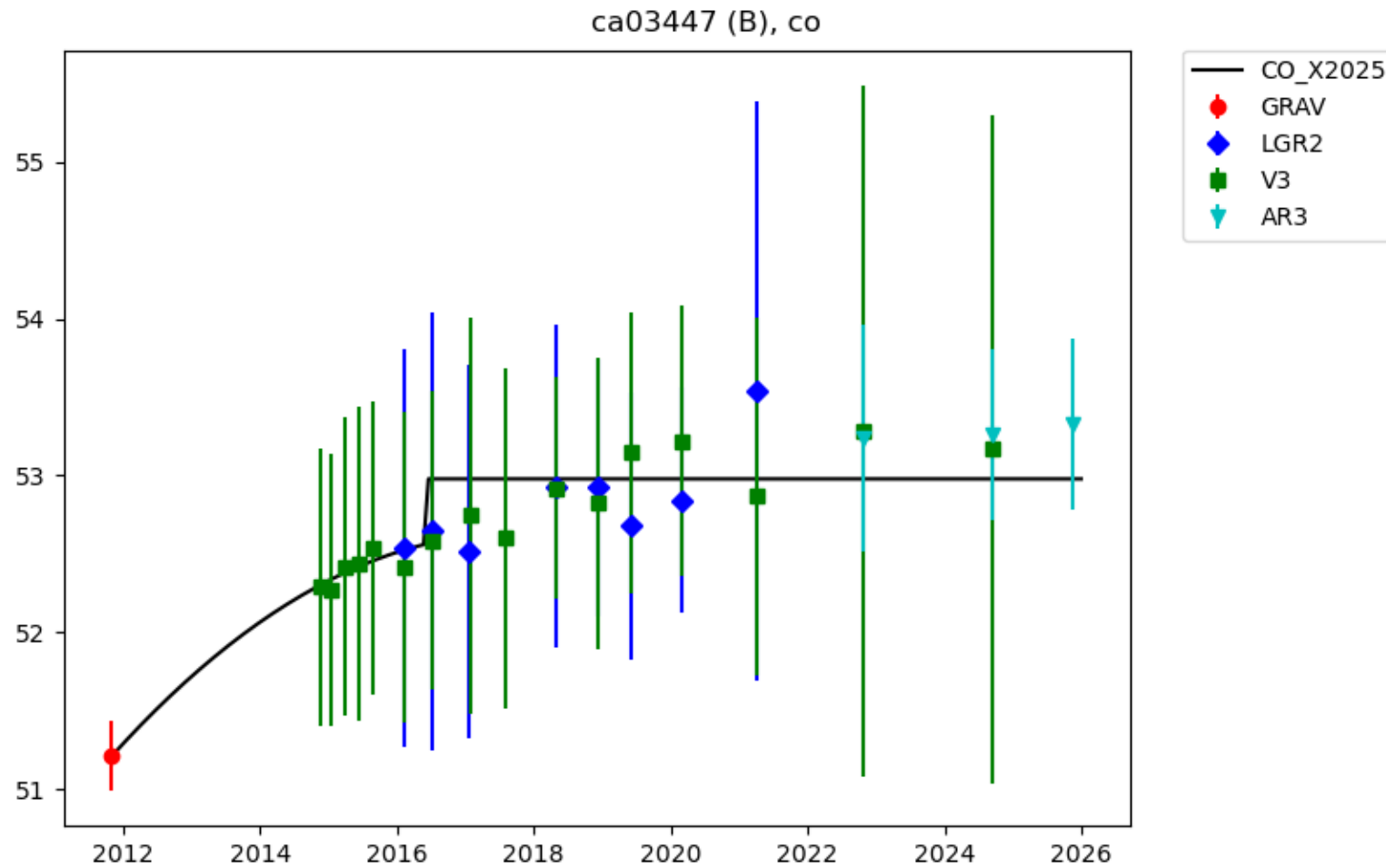
Supplemental figures

1. 2011 primary standard
2. 2015 gravimetric standards – fits with imposed 2 year data gap
3. Current secondary standards
4. 1999/2000 grav's
5. V1 secondary standards
6. 1990's RGD2 system secondaries
7. Long term target tanks

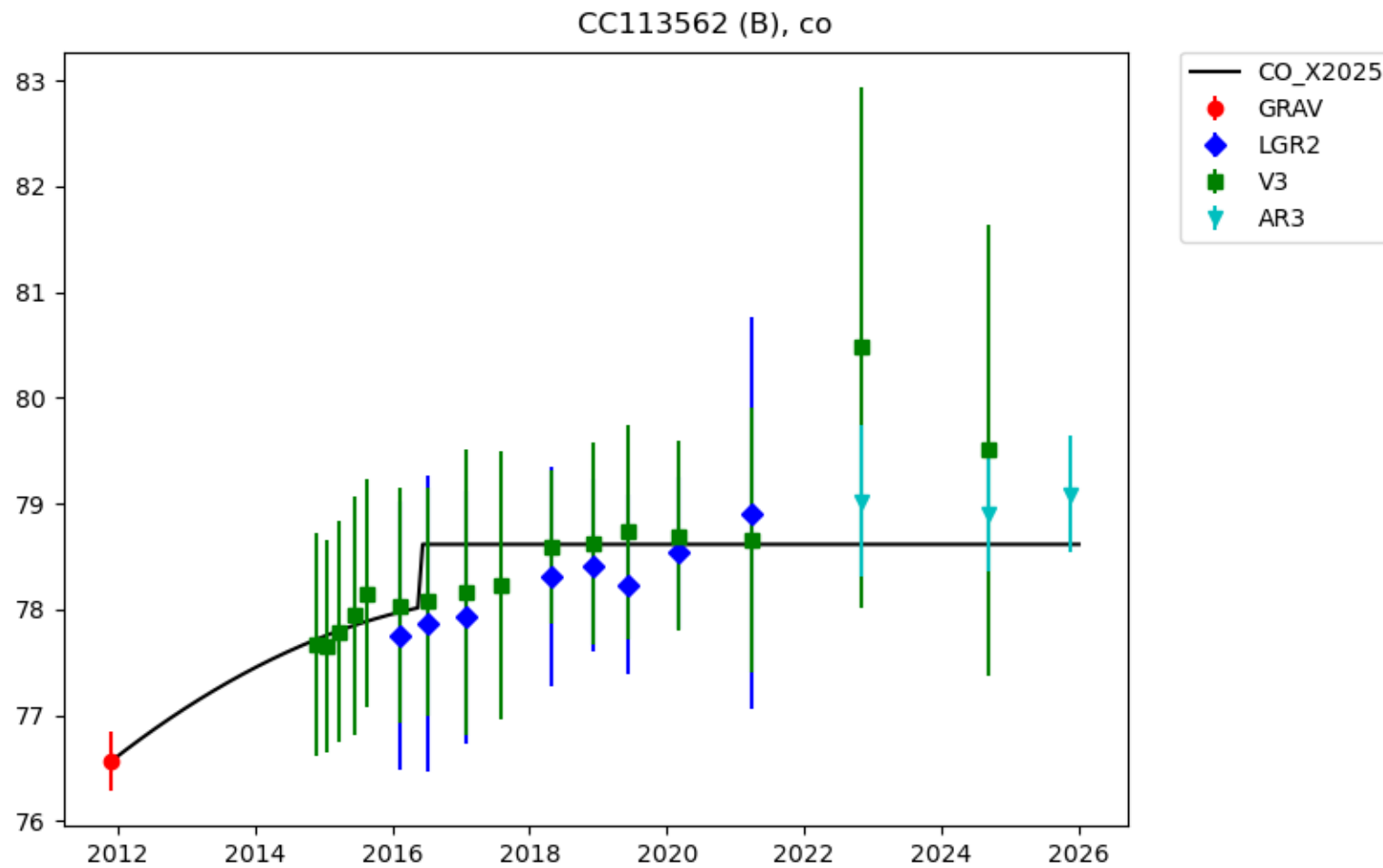
2011 primary standards – gravimetric values and measurement histories using the internal tracer method. X2025 value assignments shown by black line.



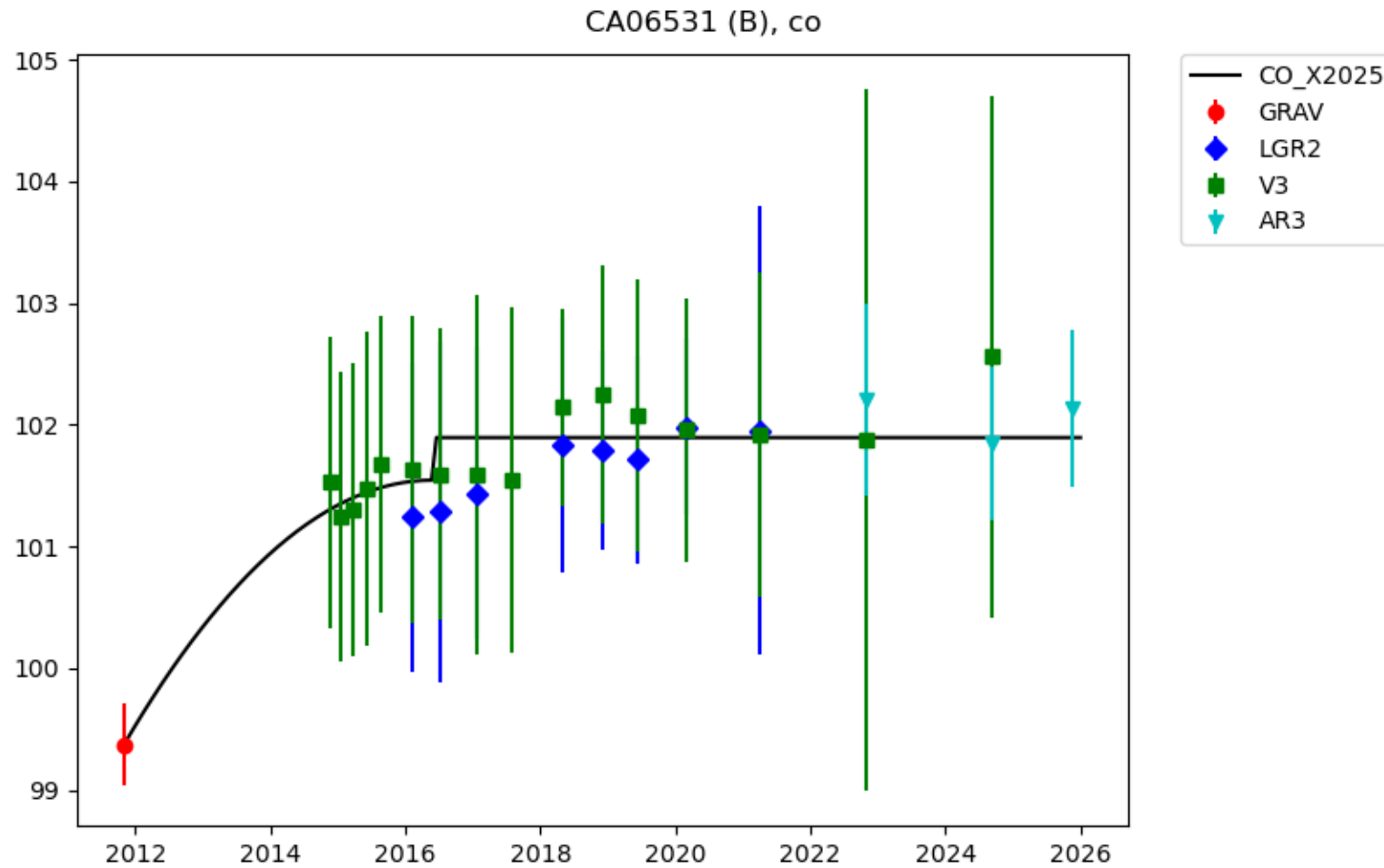
2011 primary standards – gravimetric values and measurement histories using the internal tracer method. X2025 value assignments shown by black line.



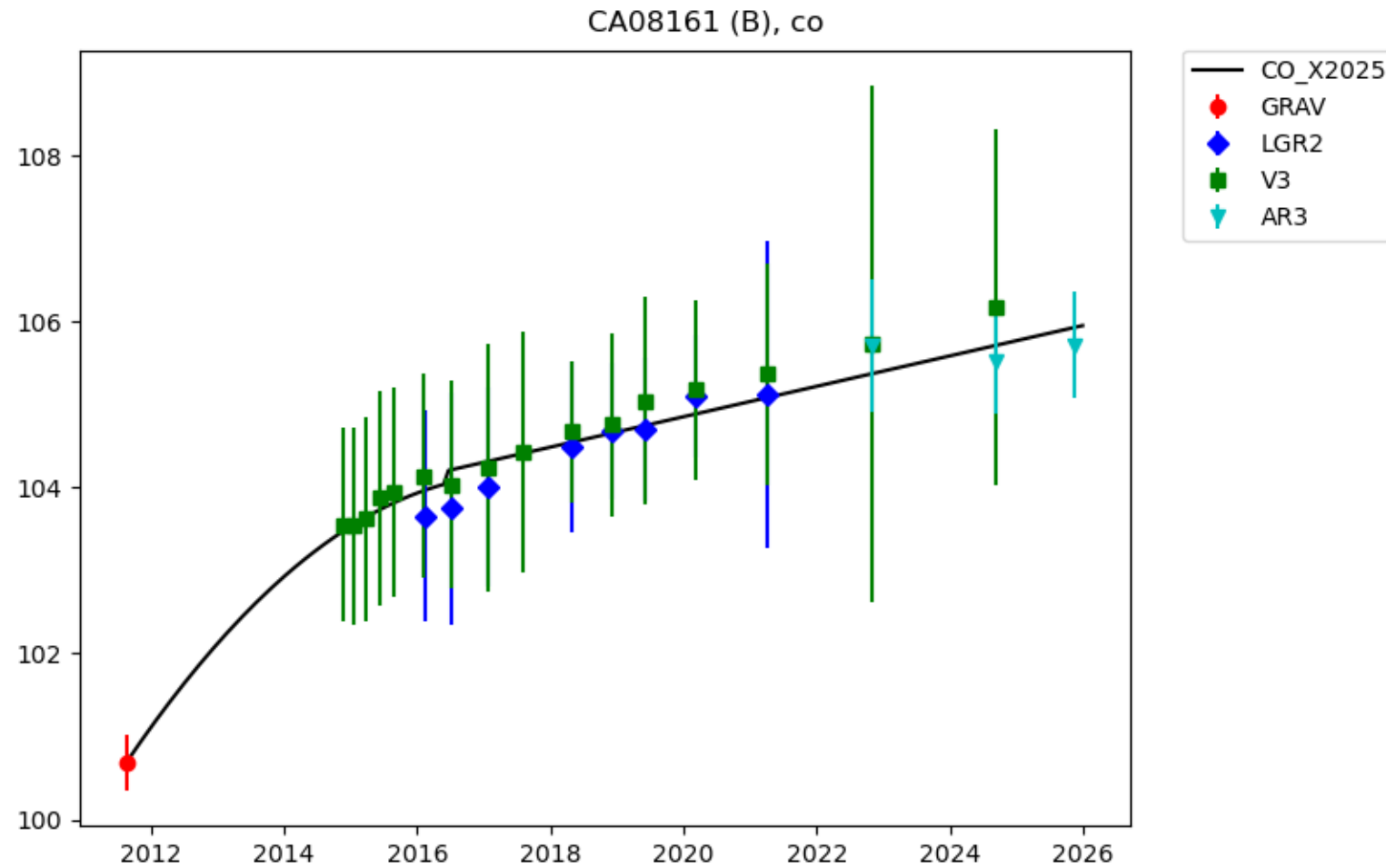
2011 primary standards – gravimetric values and measurement histories using the internal tracer method. X2025 value assignments shown by black line.



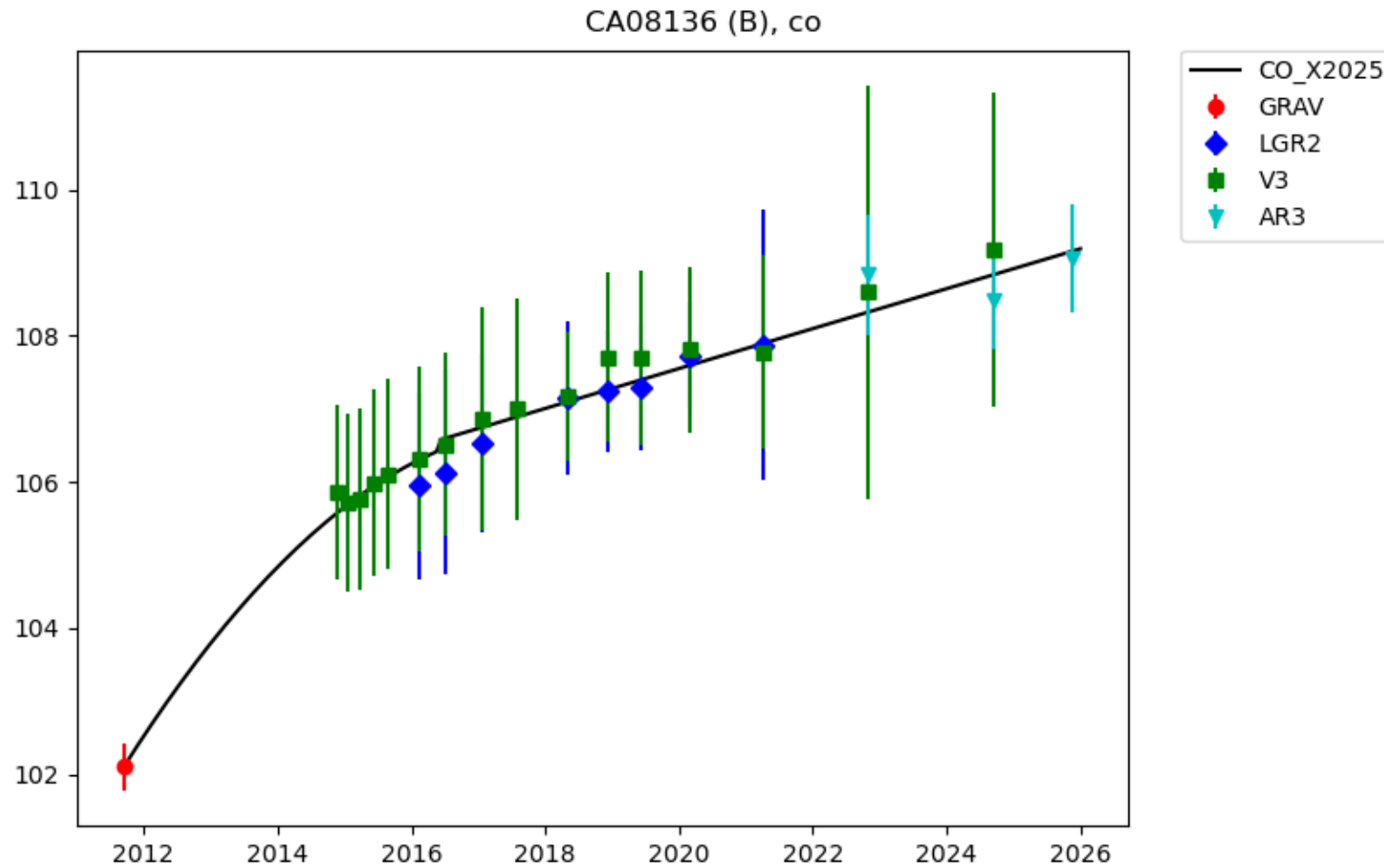
2011 primary standards – gravimetric values and measurement histories using the internal tracer method. X2025 value assignments shown by black line.



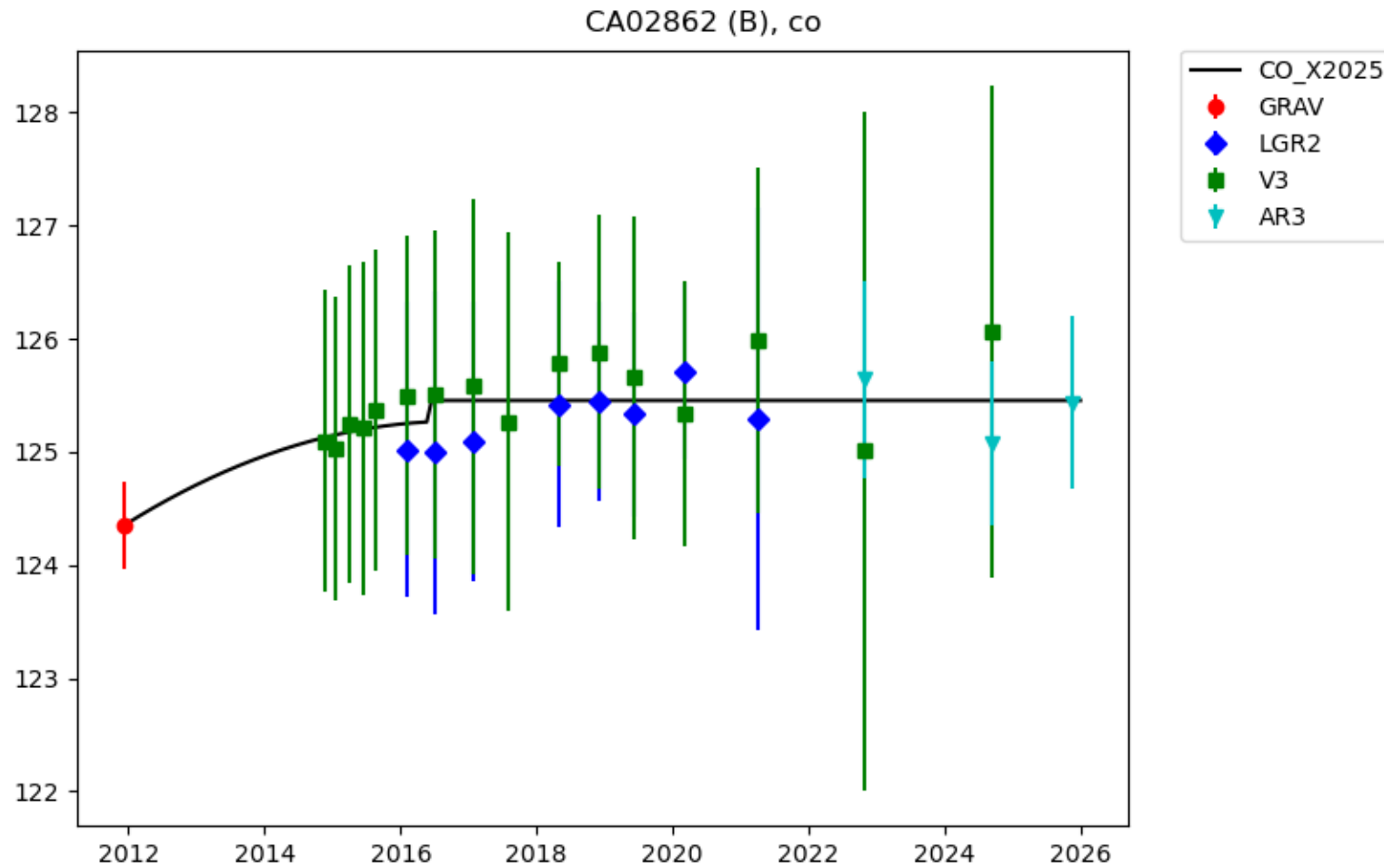
2011 primary standards – gravimetric values and measurement histories using the internal tracer method. X2025 value assignments shown by black line.



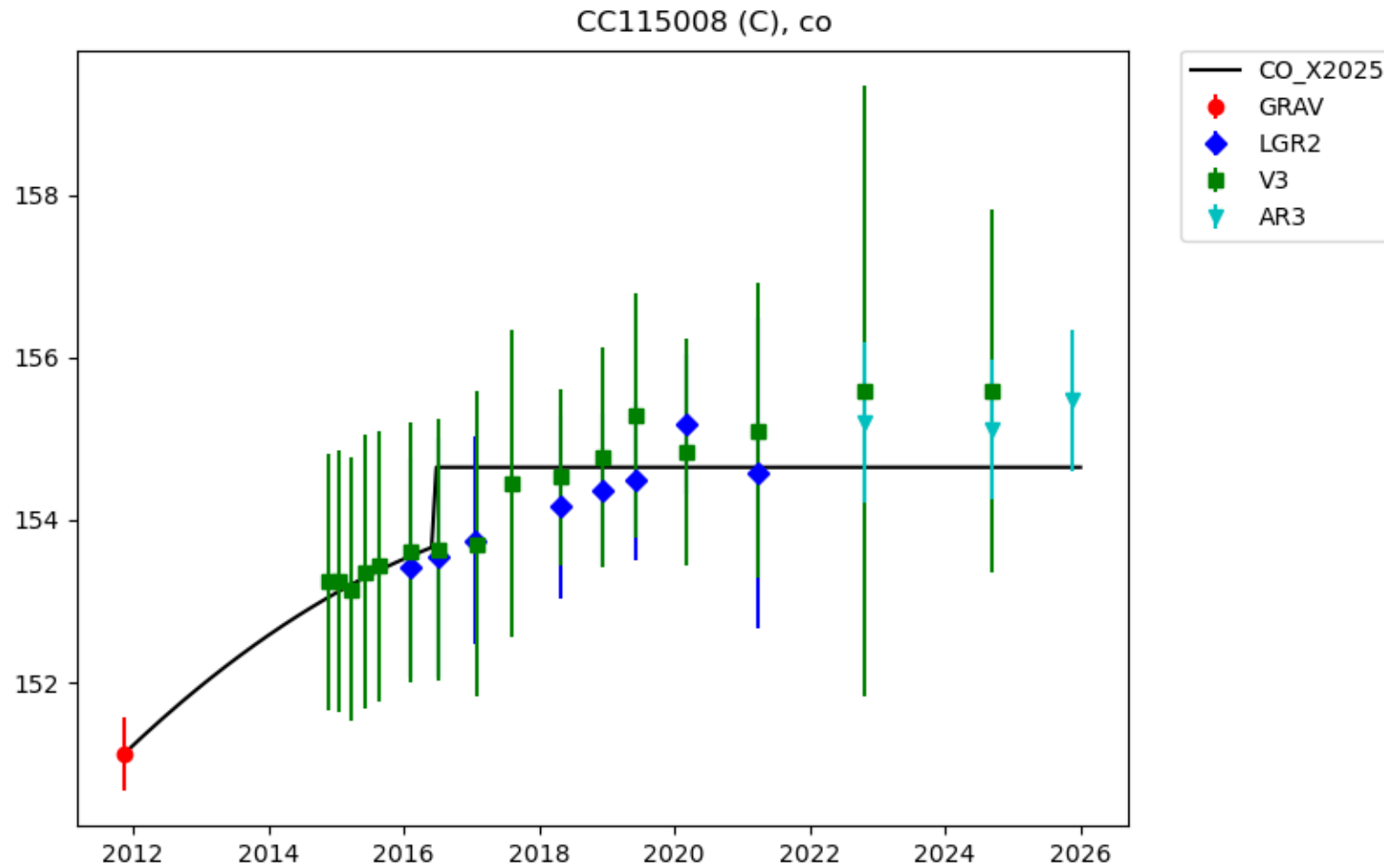
2011 primary standards – gravimetric values and measurement histories using the internal tracer method. X2025 value assignments shown by black line.



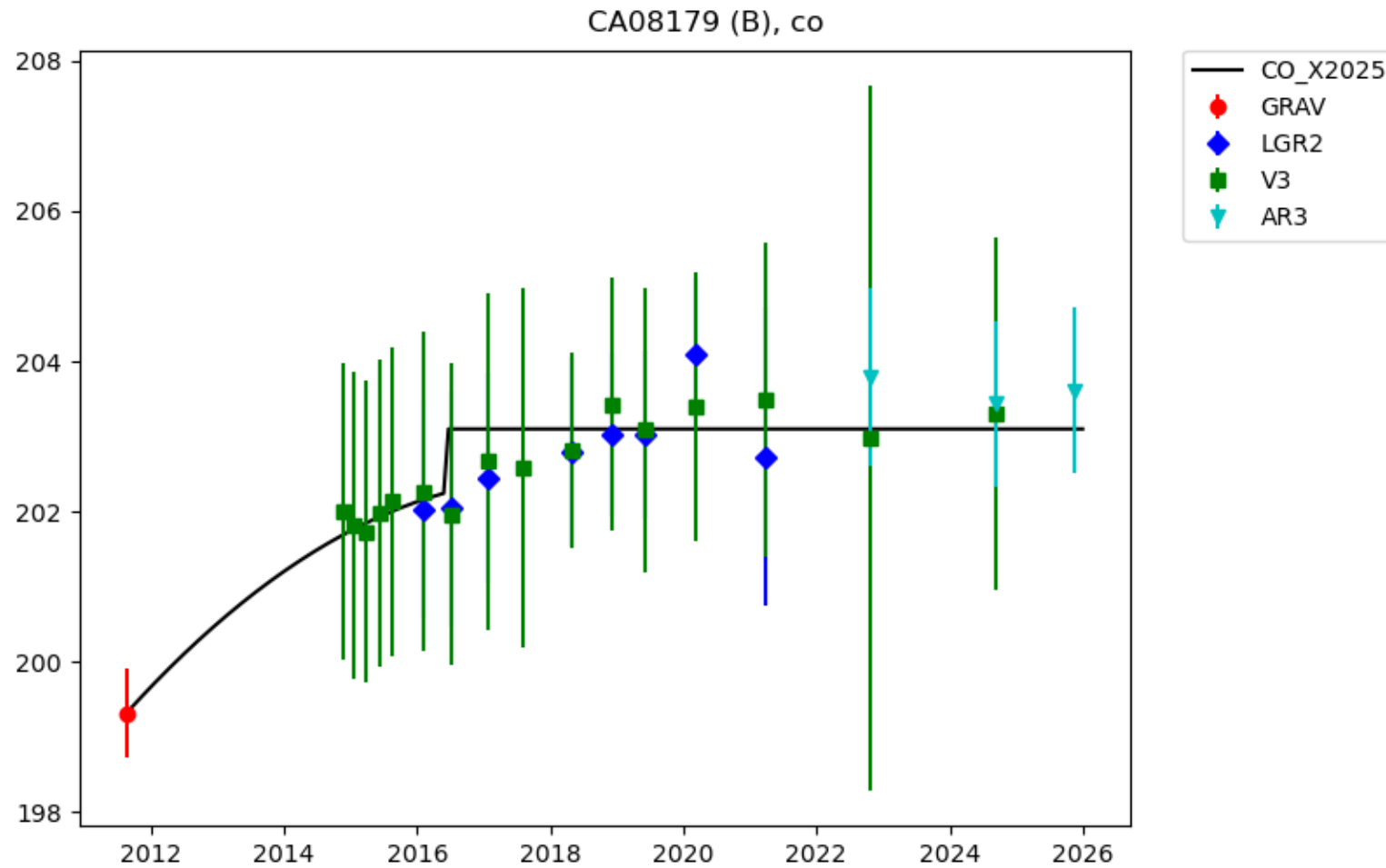
2011 primary standards – gravimetric values and measurement histories using the internal tracer method. X2025 value assignments shown by black line.



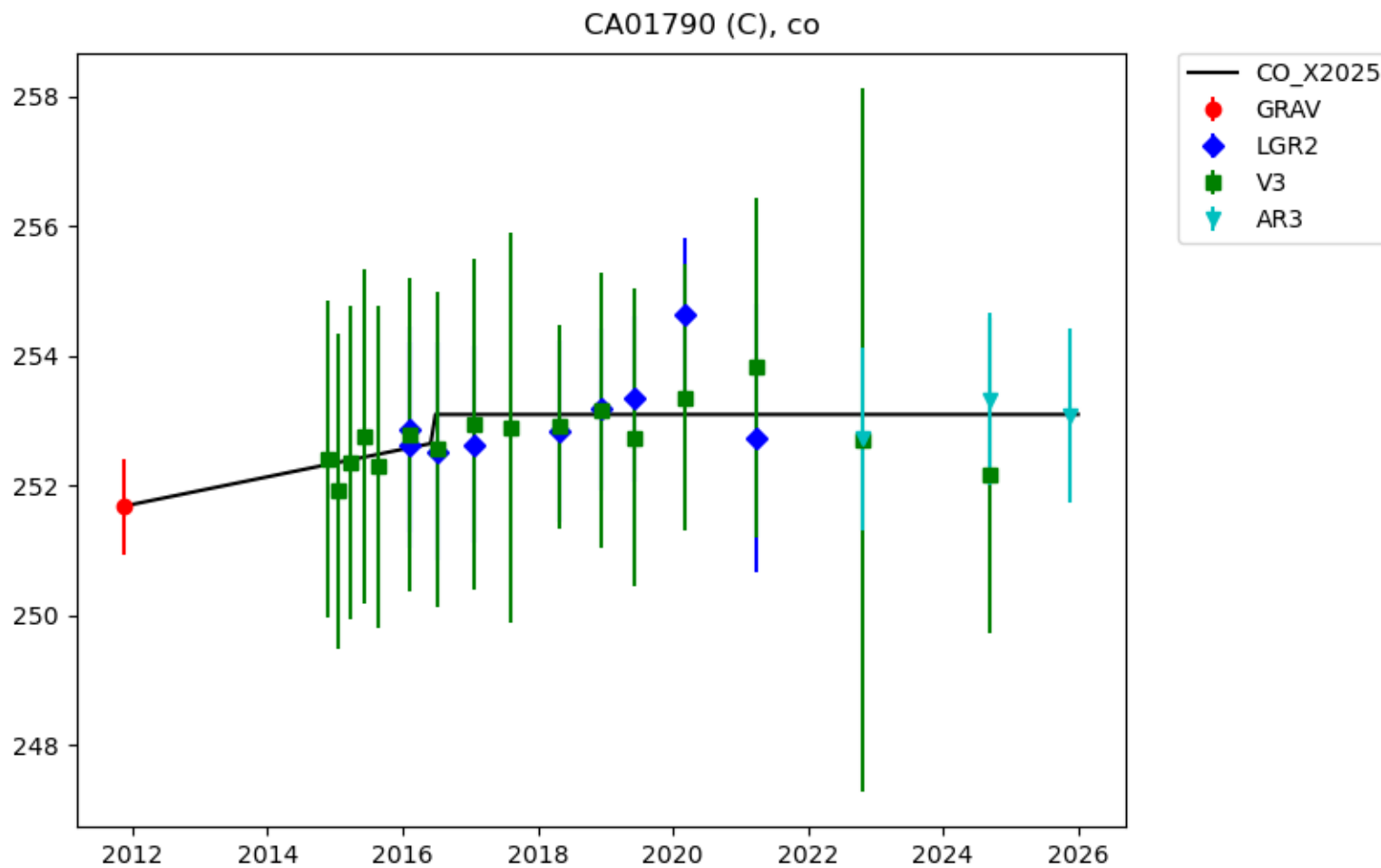
2011 primary standards – gravimetric values and measurement histories using the internal tracer method. X2025 value assignments shown by black line.



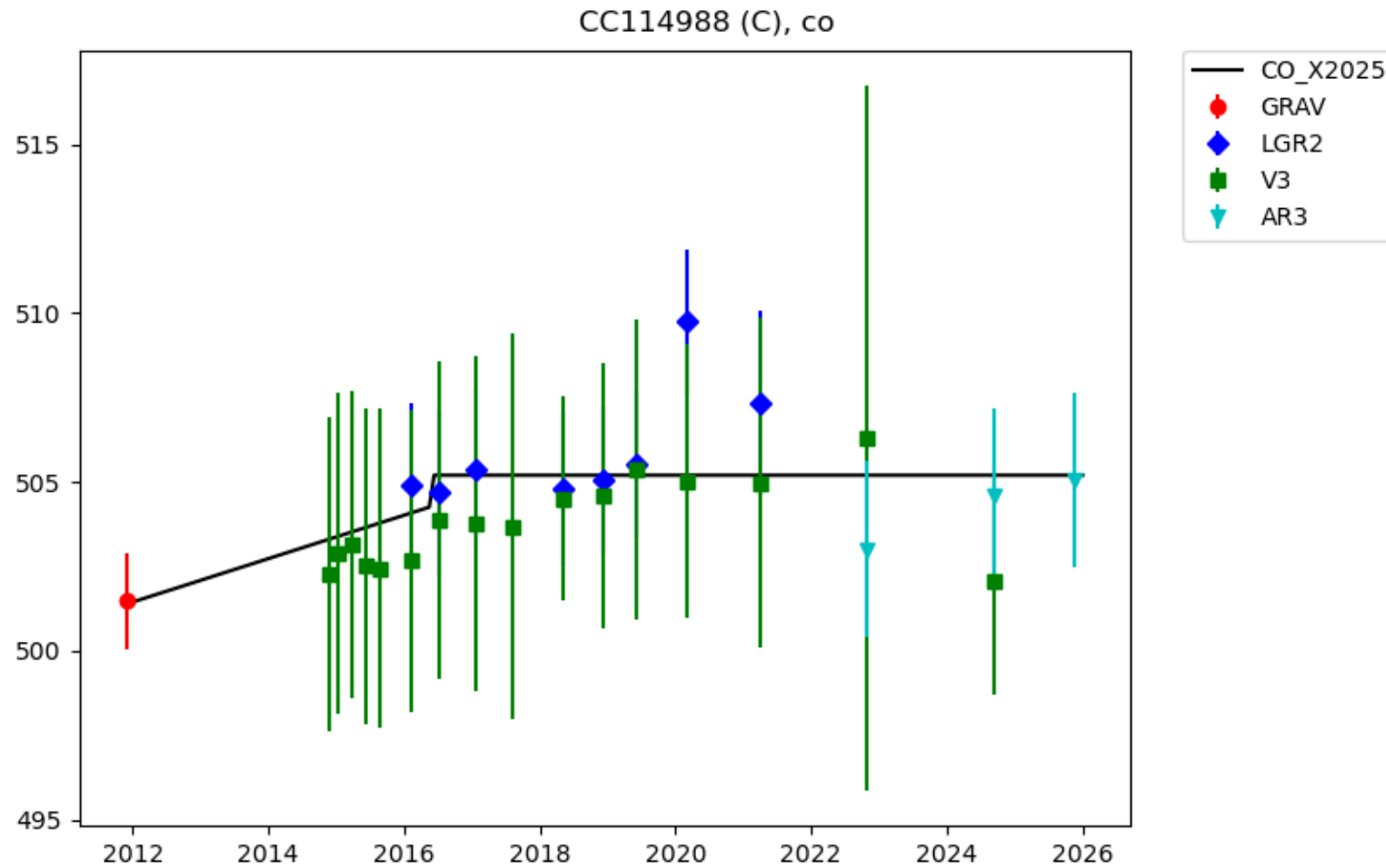
2011 primary standards – gravimetric values and measurement histories using the internal tracer method. X2025 value assignments shown by black line.



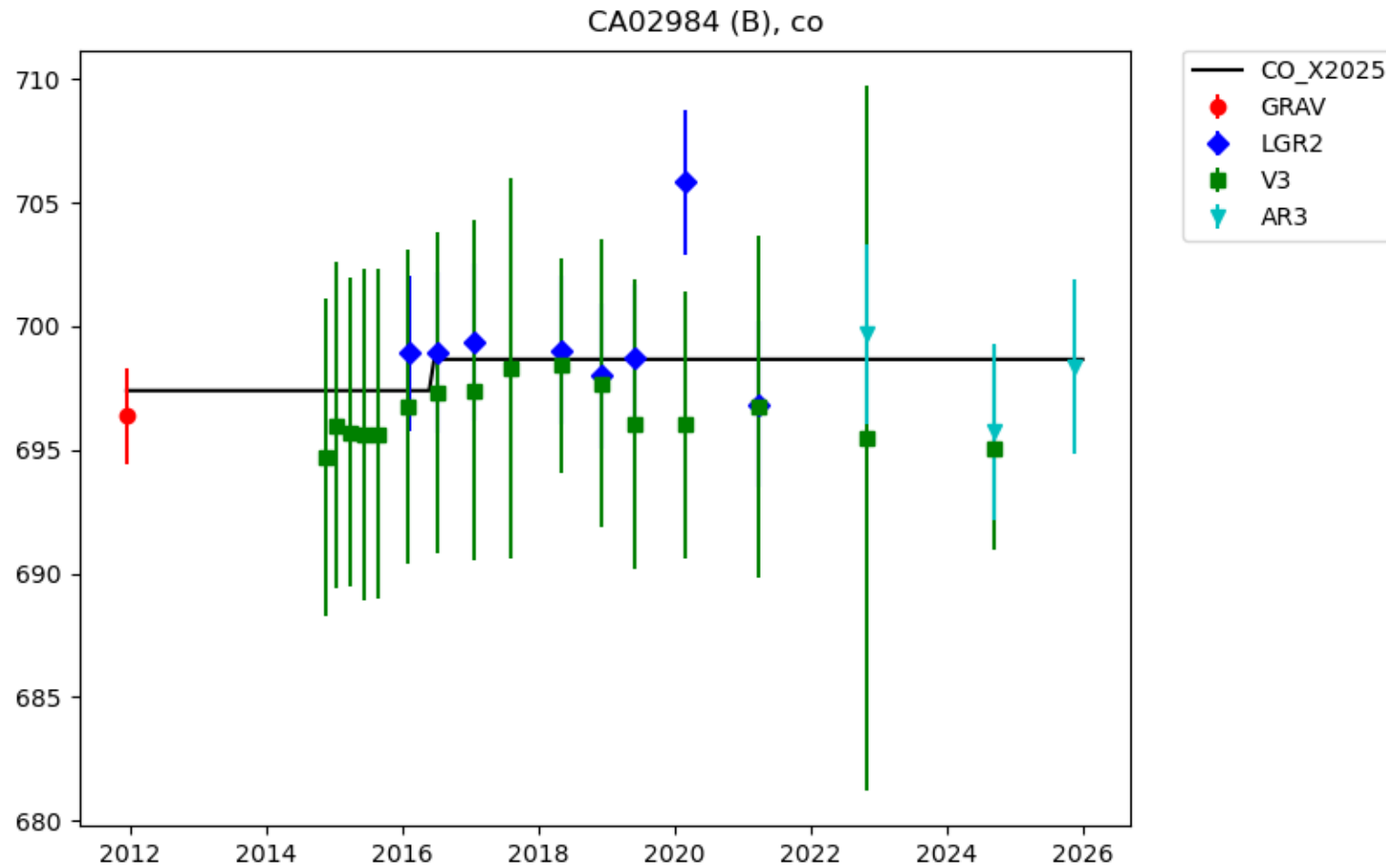
2011 primary standards – gravimetric values and measurement histories using the internal tracer method. X2025 value assignments shown by black line.



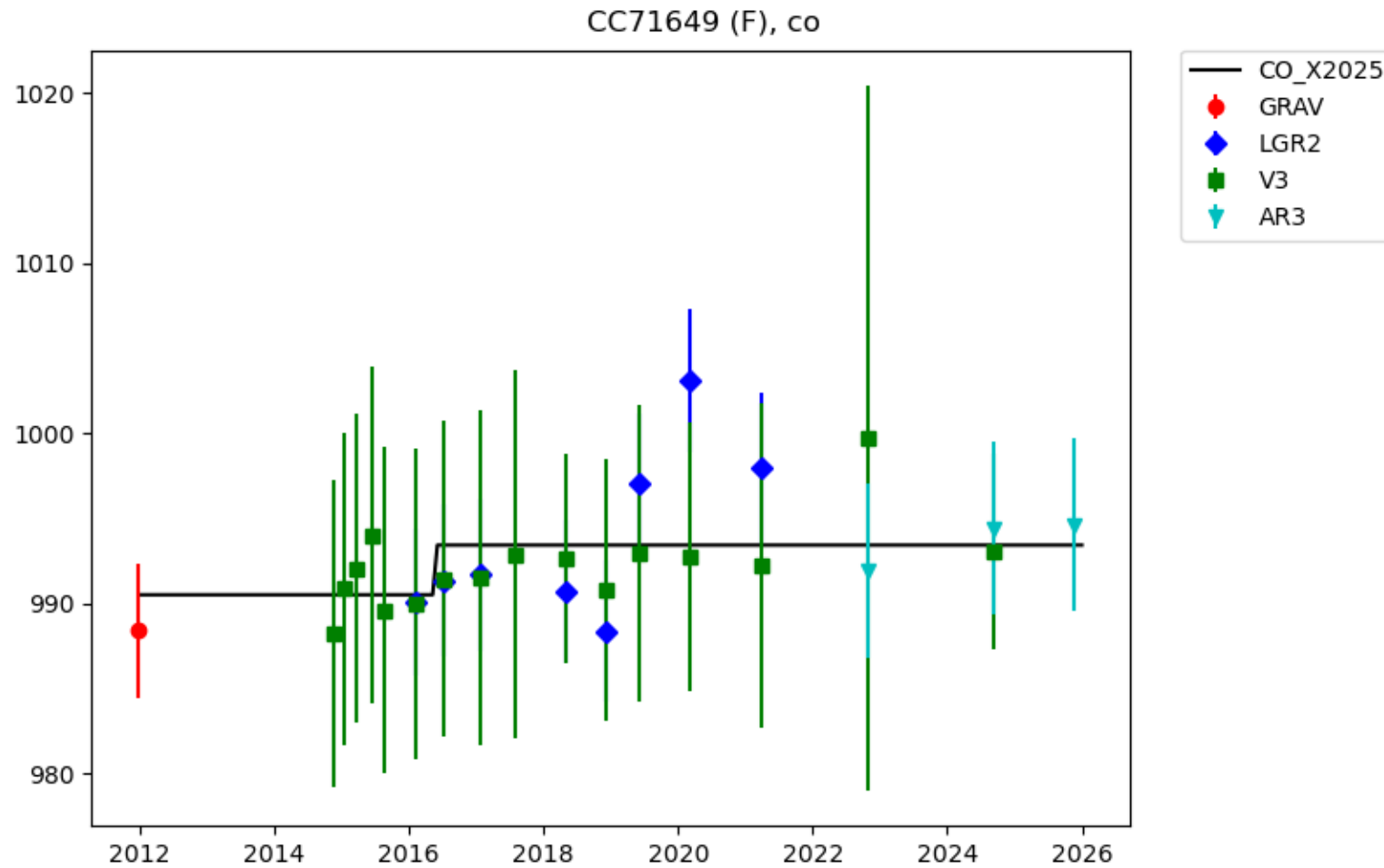
2011 primary standards – gravimetric values and measurement histories using the internal tracer method. X2025 value assignments shown by black line.



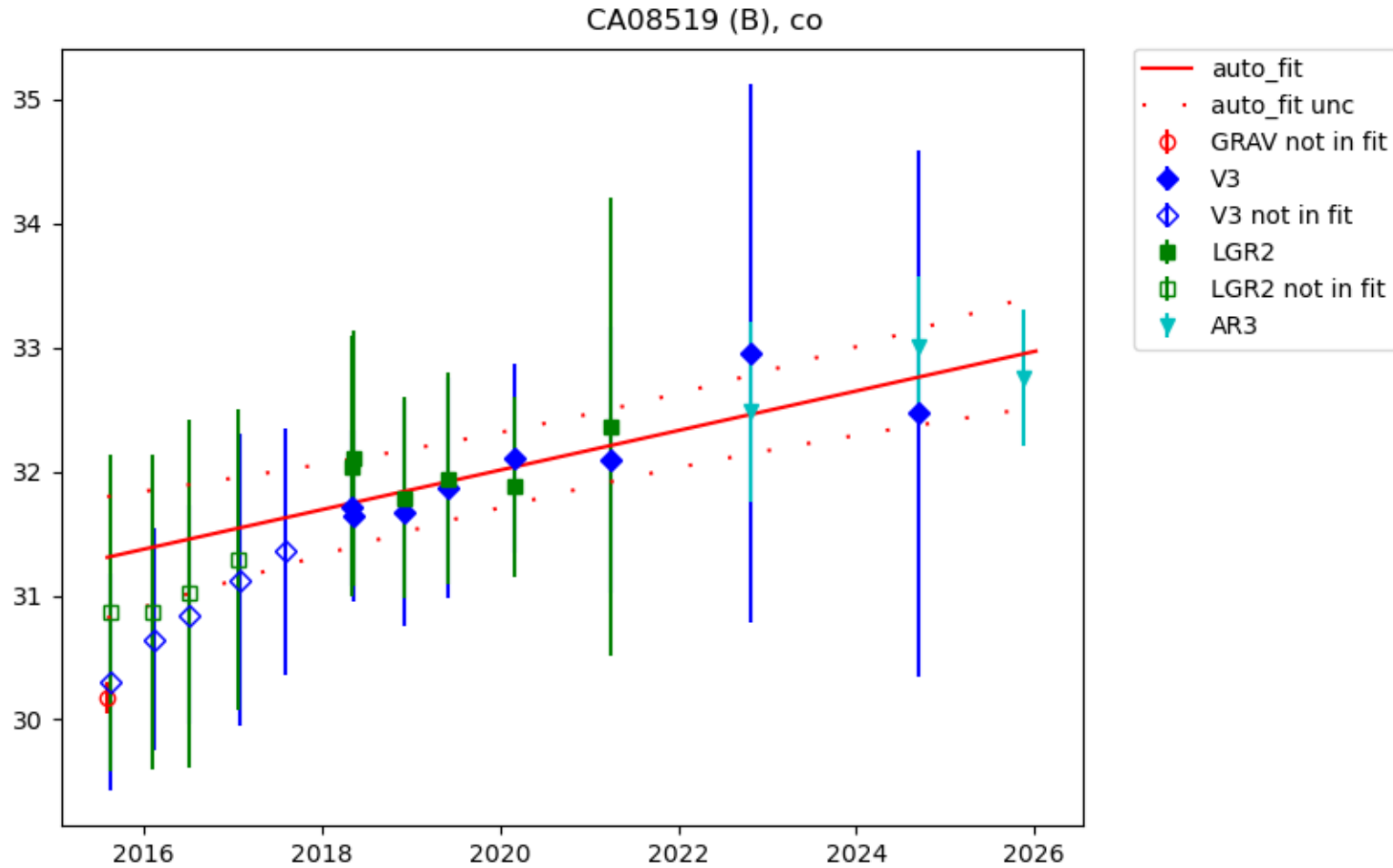
2011 primary standards – gravimetric values and measurement histories using the internal tracer method. X2025 value assignments shown by black line.



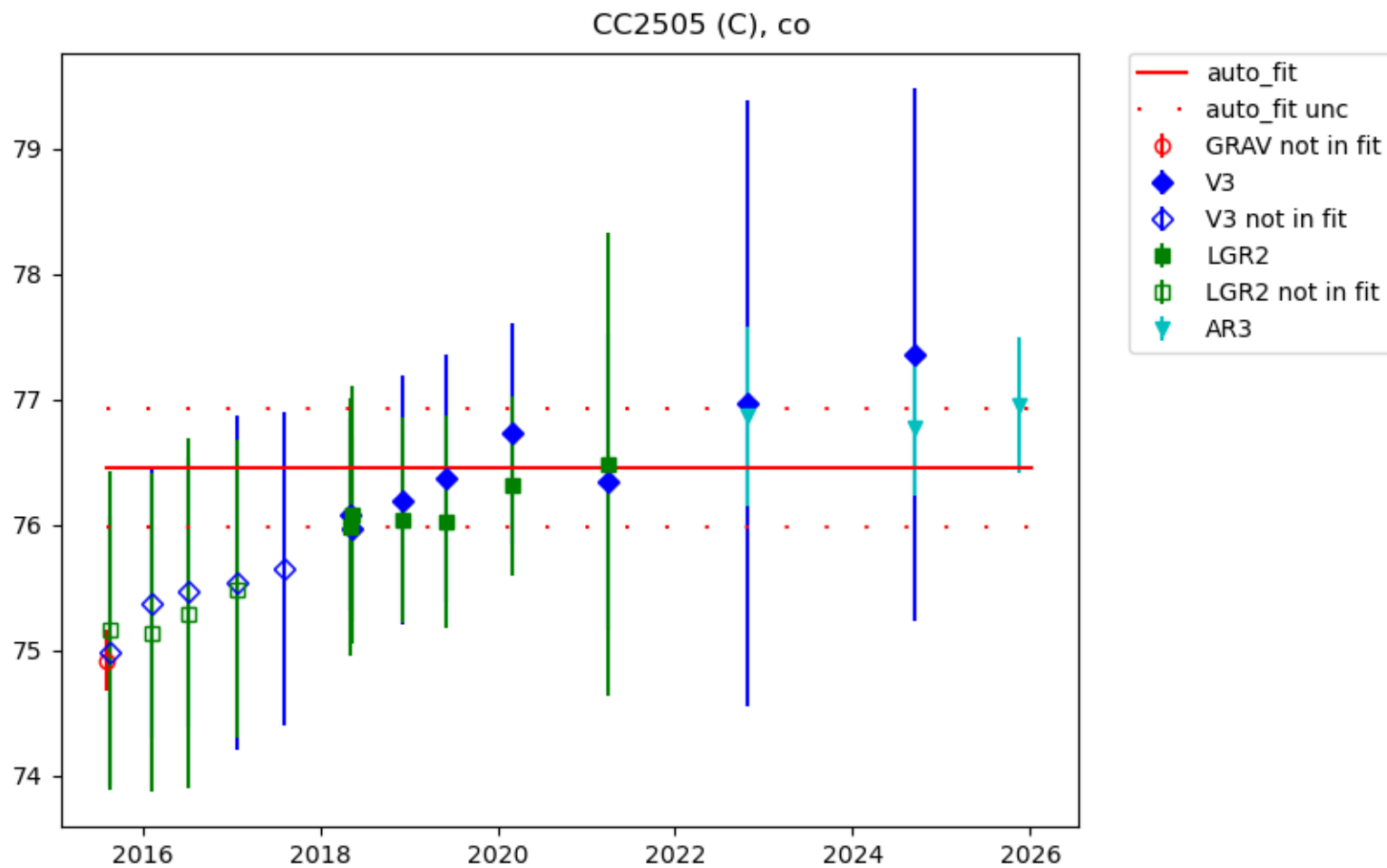
2011 primary standards – gravimetric values and measurement histories using the internal tracer method. X2025 value assignments shown by black line.



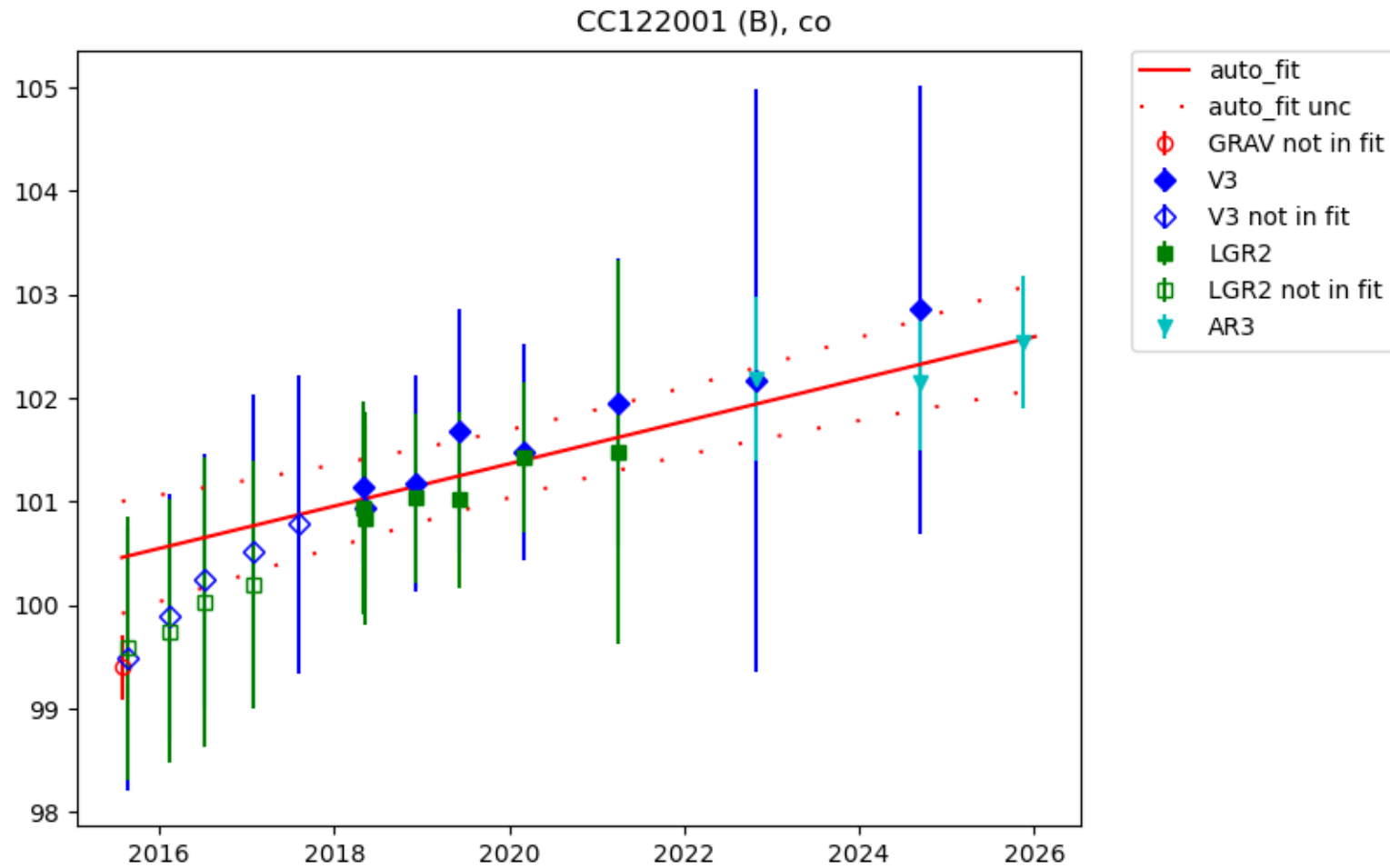
2015 gravimetric standards. Gravimetric value and all measurements vs the dilution standards shown. Fit it to the measurement data with 2.5 year data gap imposed. Open symbols are not included in the fits.



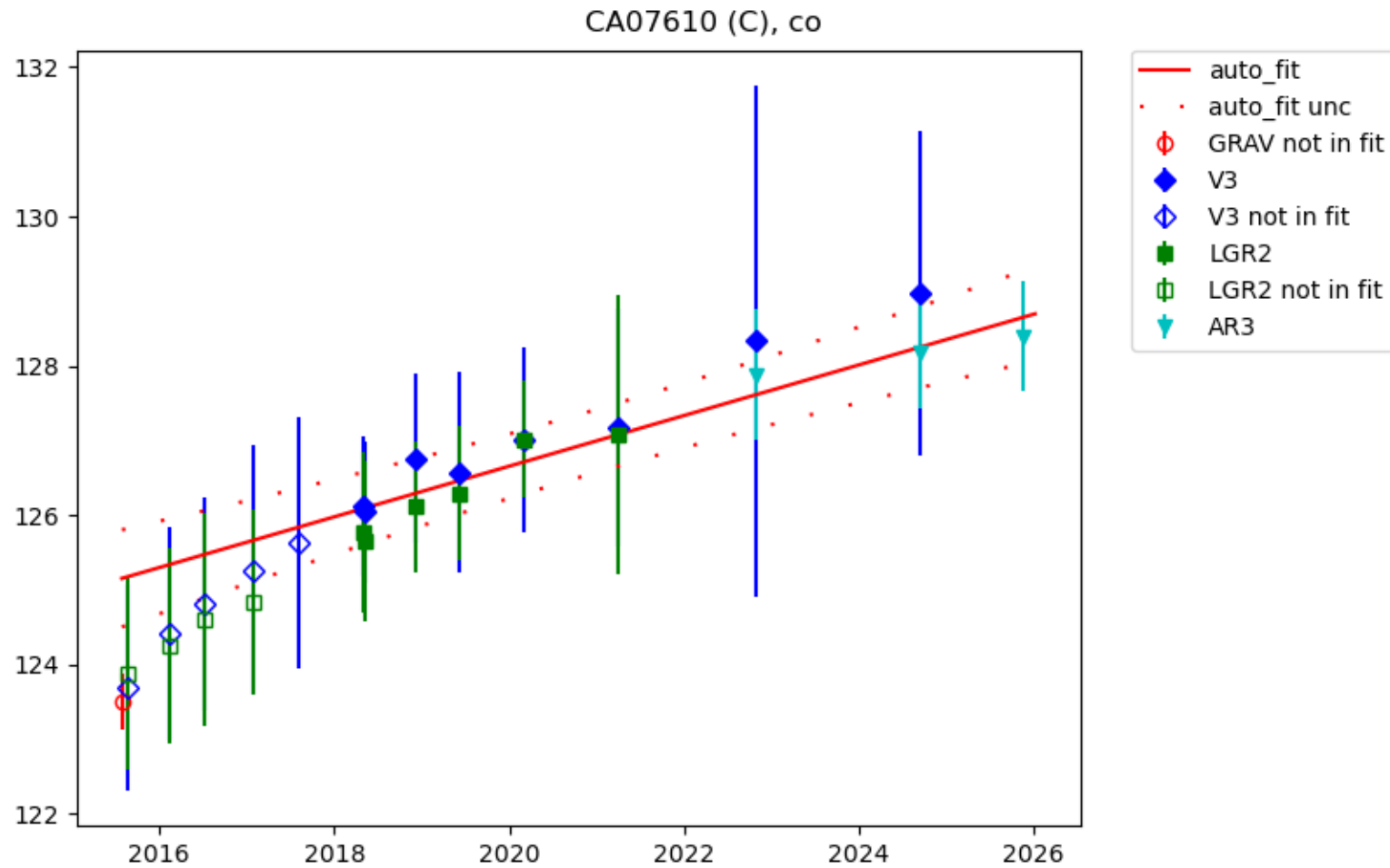
2015 gravimetric standards. Gravimetric value and all measurements vs the dilution standards shown. Fit it to the measurement data with 2.5 year data gap imposed. Open symbols are not included in the fits.



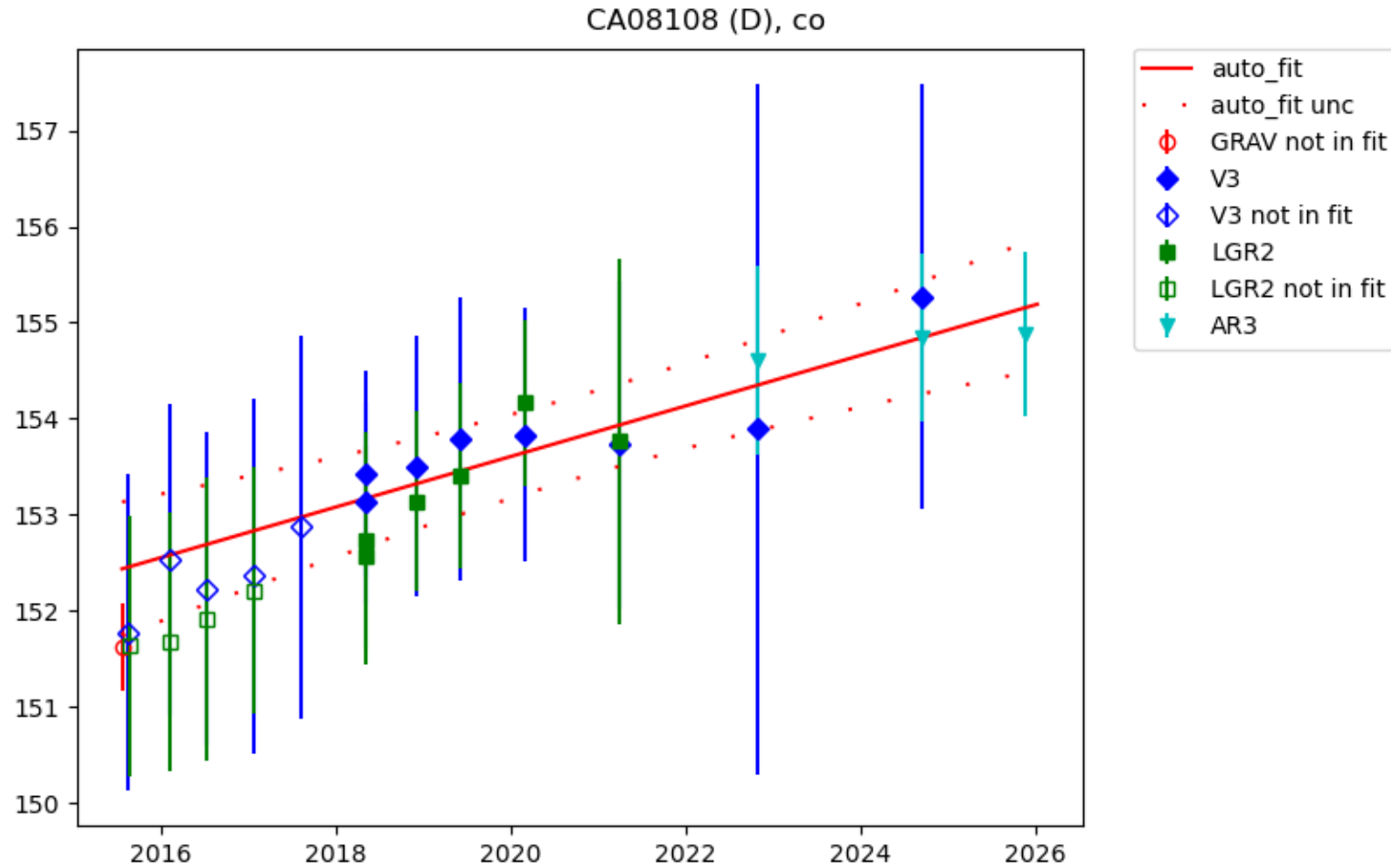
2015 gravimetric standards. Gravimetric value and all measurements vs the dilution standards shown. Fit it to the measurement data with 2.5 year data gap imposed. Open symbols are not included in the fits.



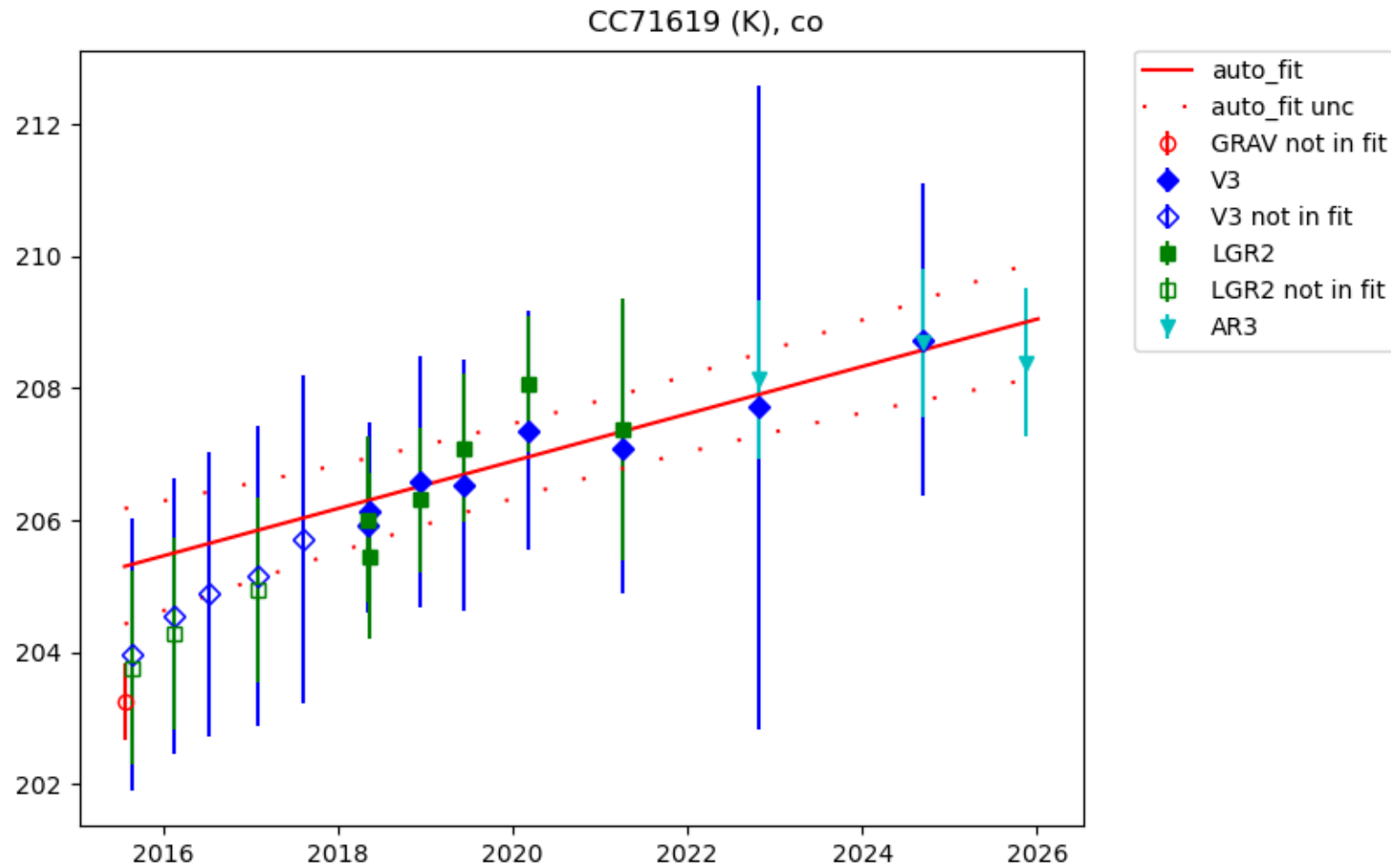
2015 gravimetric standards. Gravimetric value and all measurements vs the dilution standards shown. Fit it to the measurement data with 2.5 year data gap imposed. Open symbols are not included in the fits.



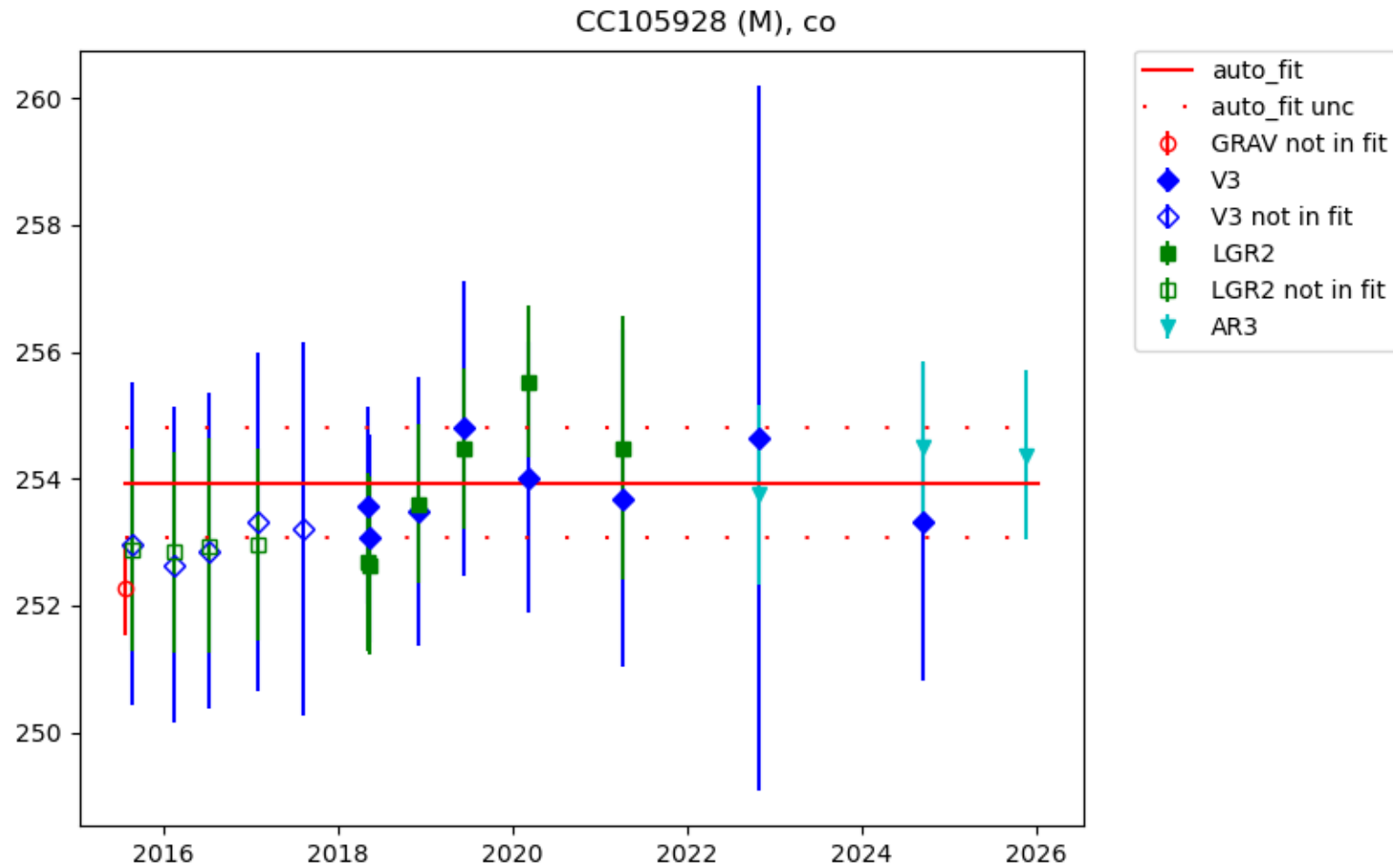
2015 gravimetric standards. Gravimetric value and all measurements vs the dilution standards shown. Fit it to the measurement data with 2.5 year data gap imposed. Open symbols are not included in the fits.



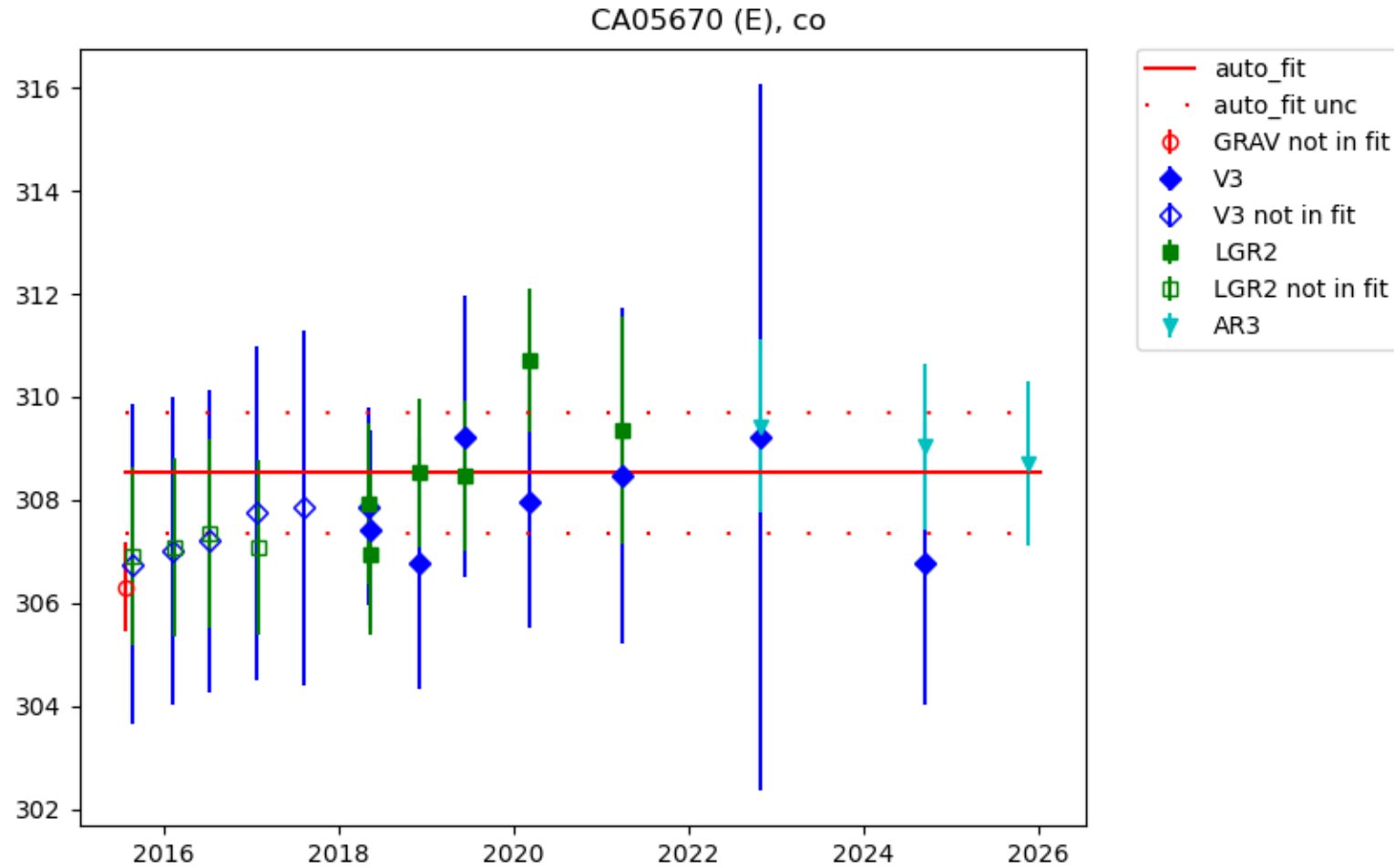
2015 gravimetric standards. Gravimetric value and all measurements vs the dilution standards shown. Fit it to the measurement data with 2.5 year data gap imposed. Open symbols are not included in the fits.



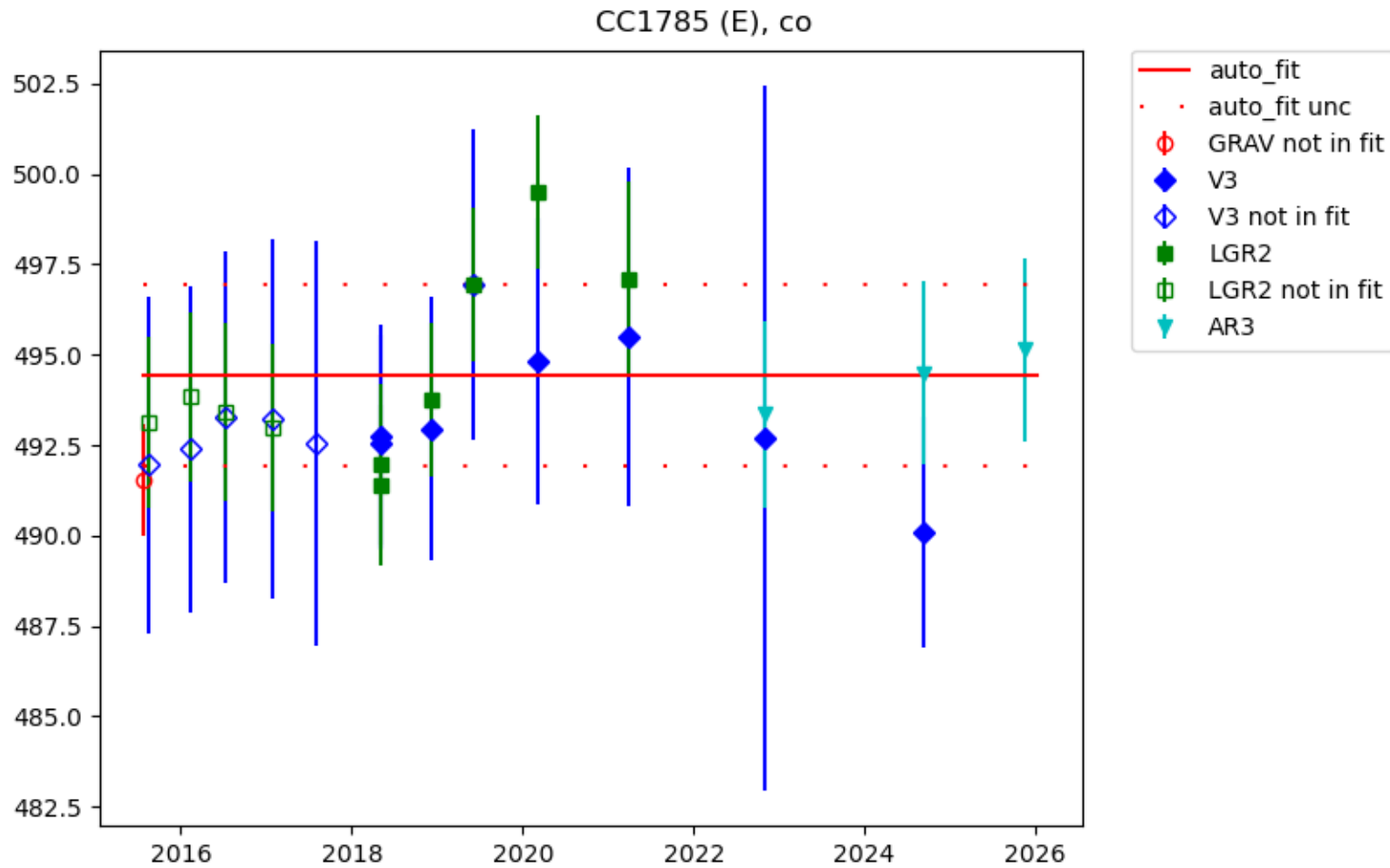
2015 gravimetric standards. Gravimetric value and all measurements vs the dilution standards shown. Fit it to the measurement data with 2.5 year data gap imposed. Open symbols are not included in the fits.



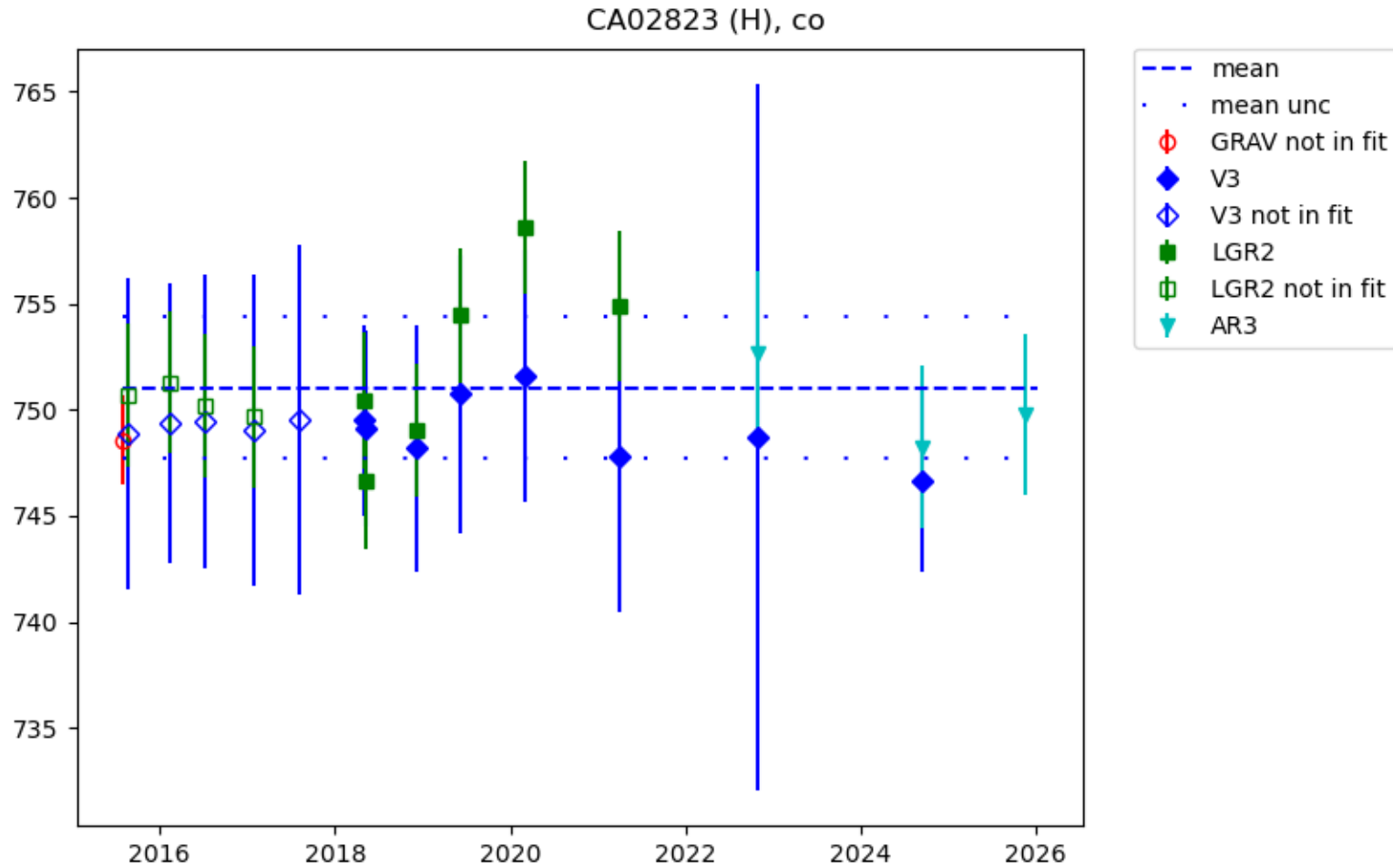
2015 gravimetric standards. Gravimetric value and all measurements vs the dilution standards shown. Fit it to the measurement data with 2.5 year data gap imposed. Open symbols are not included in the fits.



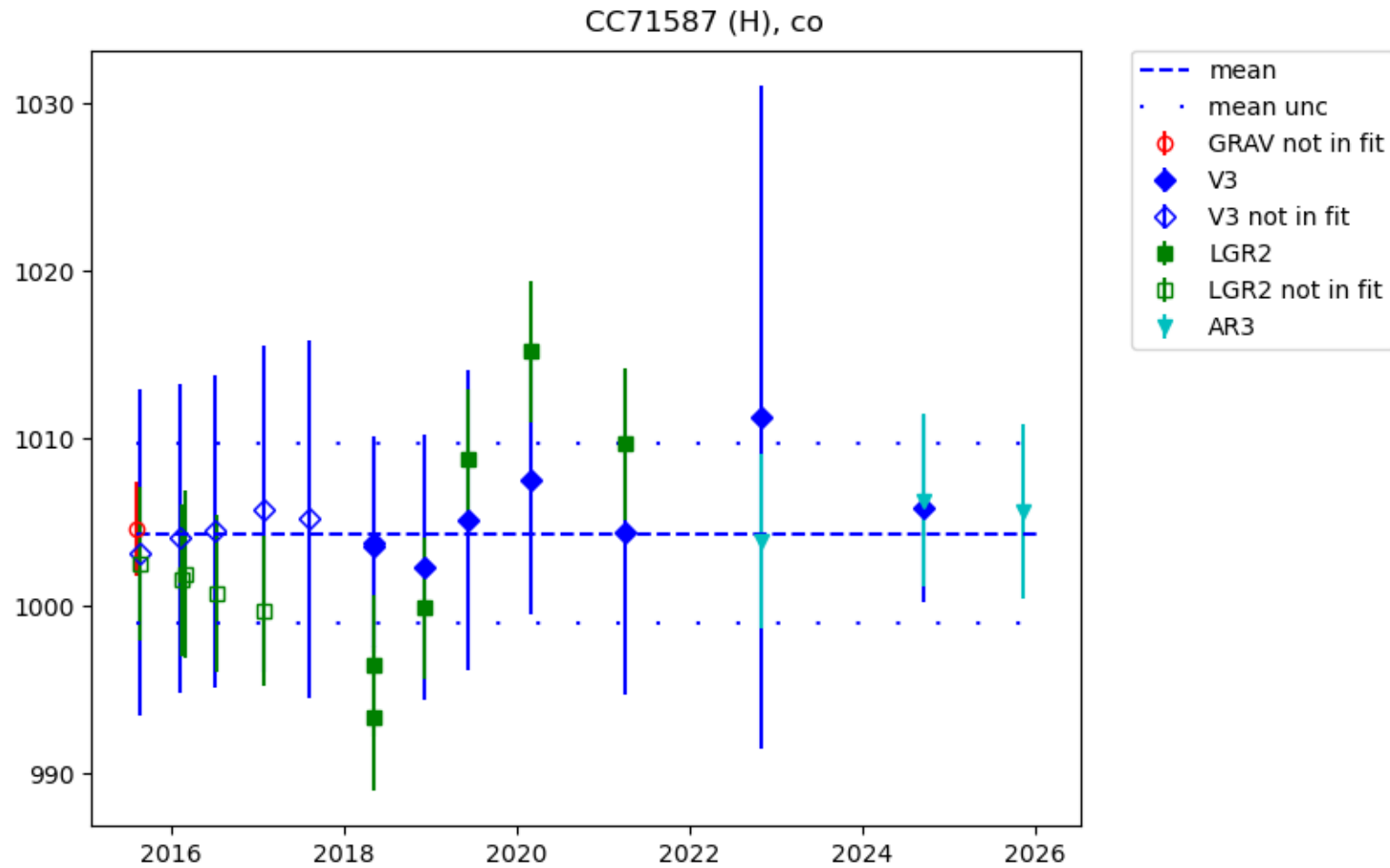
2015 gravimetric standards. Gravimetric value and all measurements vs the dilution standards shown. Fit it to the measurement data with 2.5 year data gap imposed. Open symbols are not included in the fits.



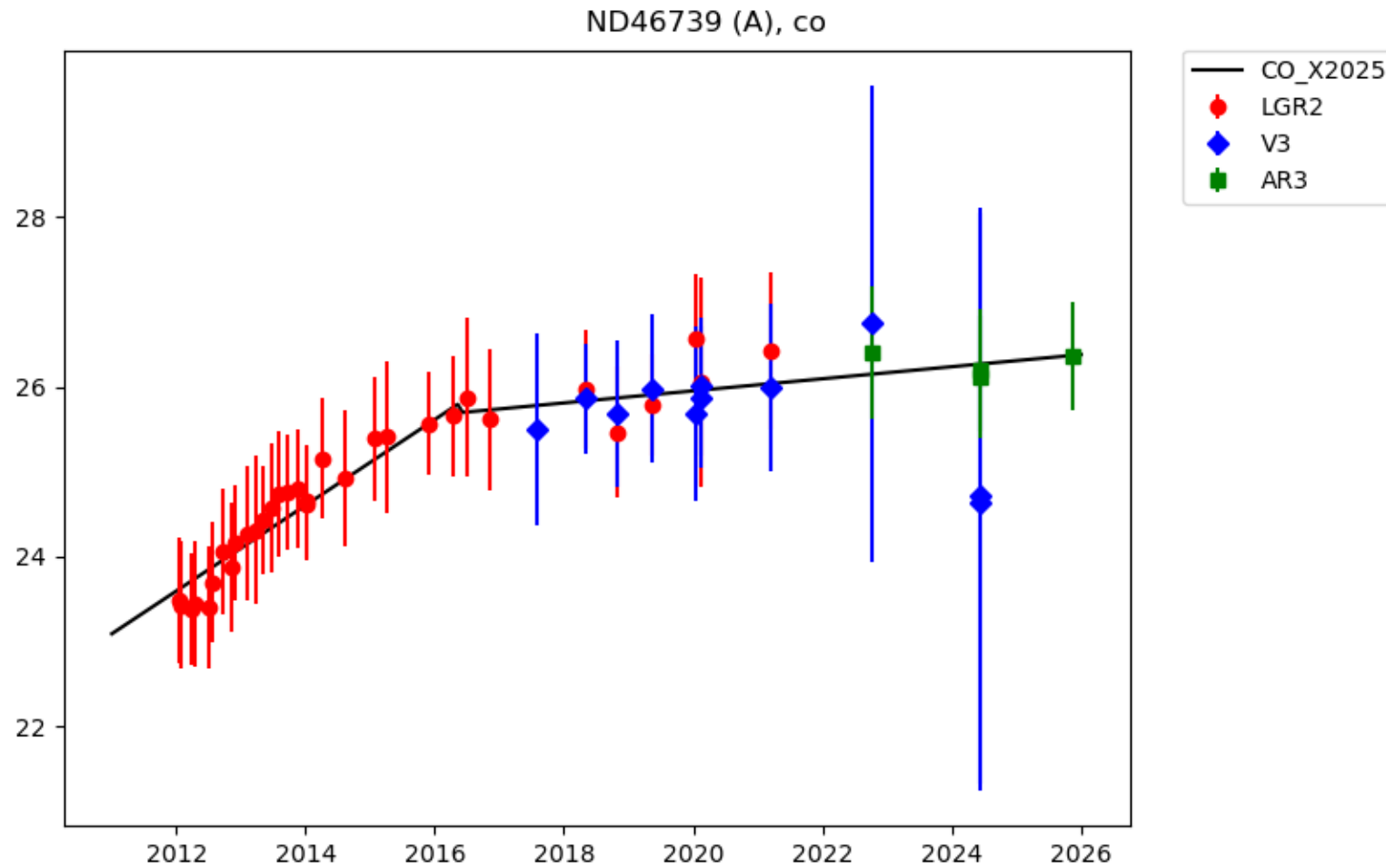
2015 gravimetric standards. Gravimetric value and all measurements vs the dilution standards shown. Fit it to the measurement data with 2.5 year data gap imposed. Open symbols are not included in the fits.



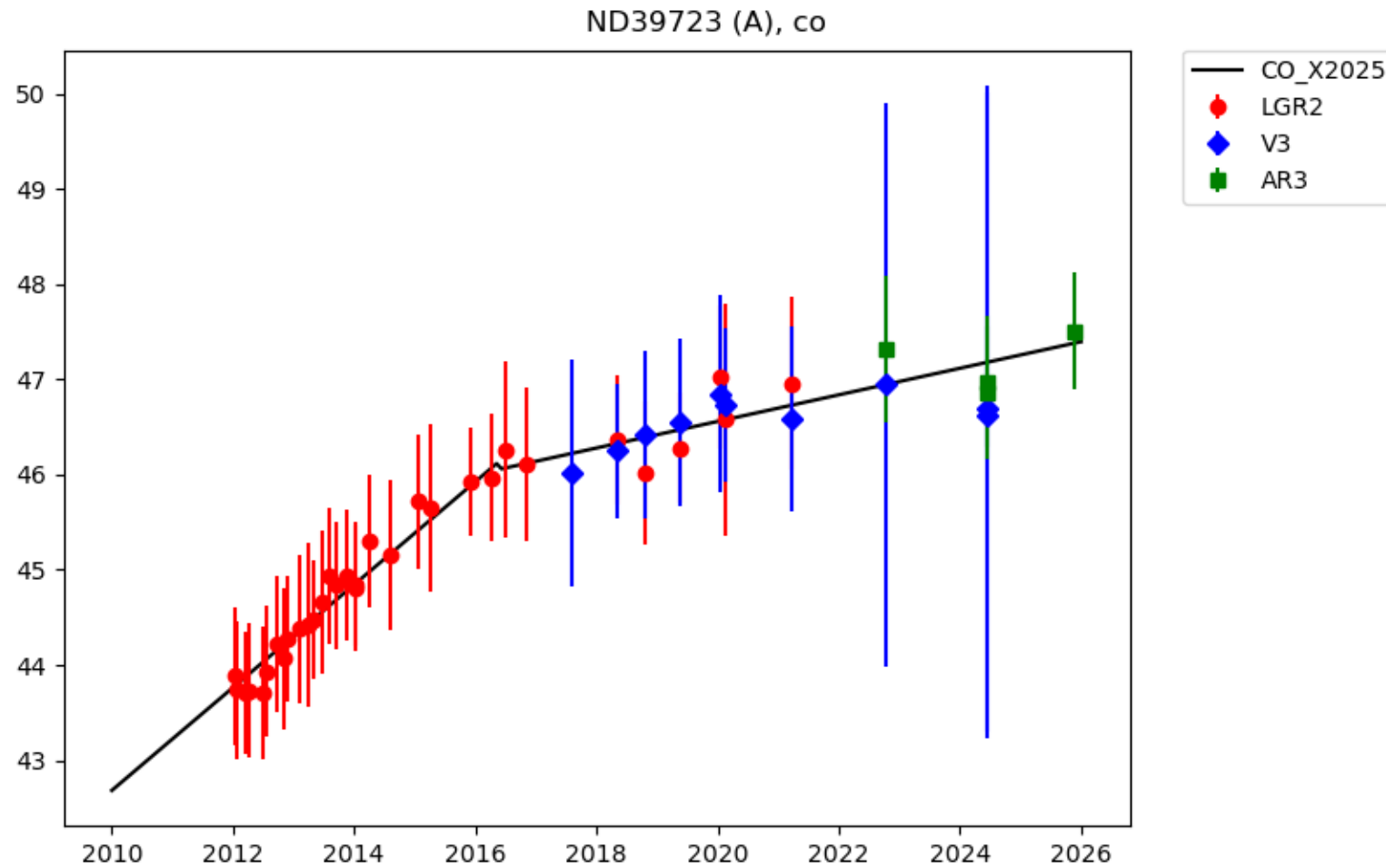
2015 gravimetric standards. Gravimetric value and all measurements vs the dilution standards shown. Fit it to the measurement data with 2.5 year data gap imposed. Open symbols are not included in the fits.



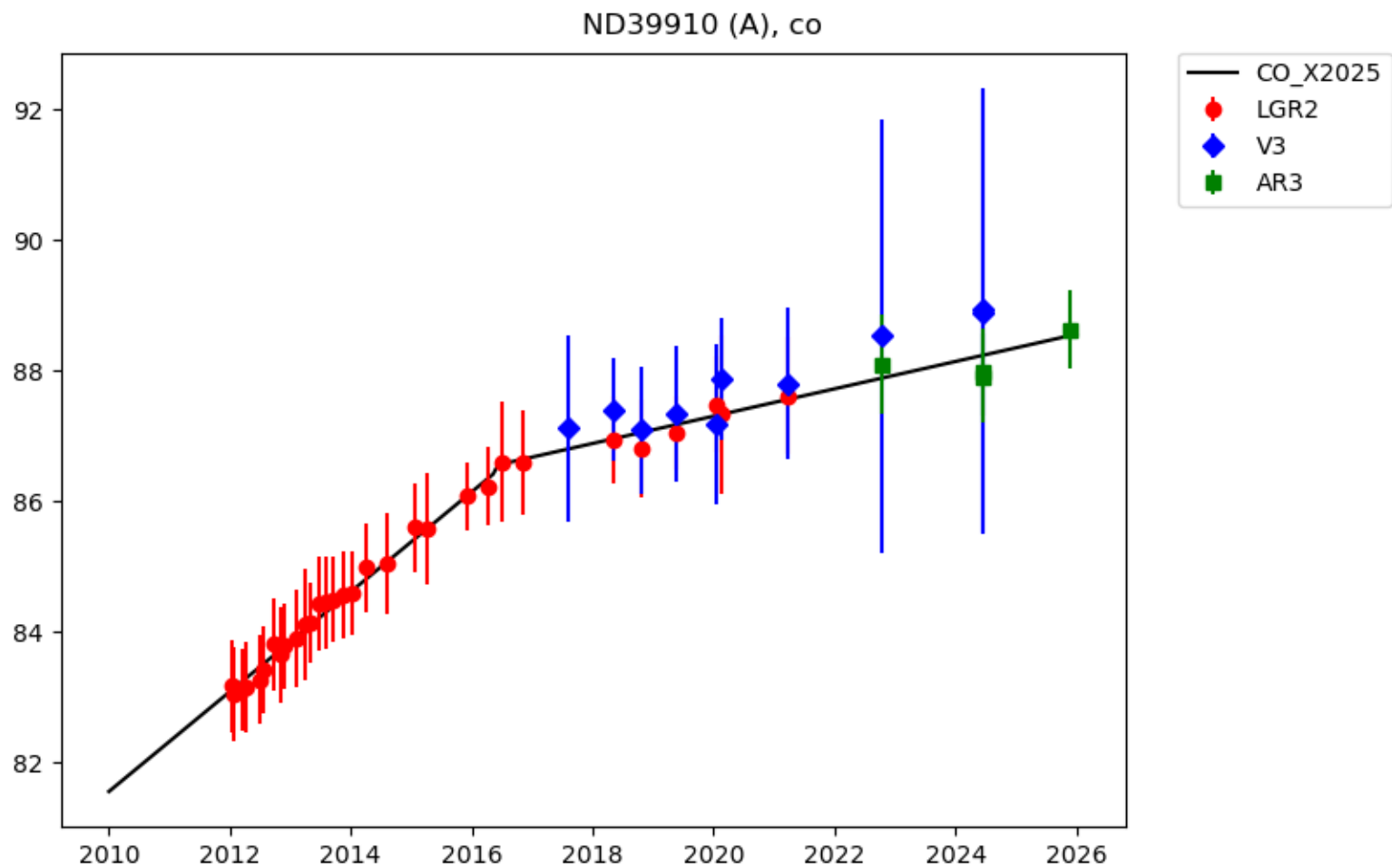
Current secondary standards – all data used for value assignments are calibrations versus the 2011 primary standards.



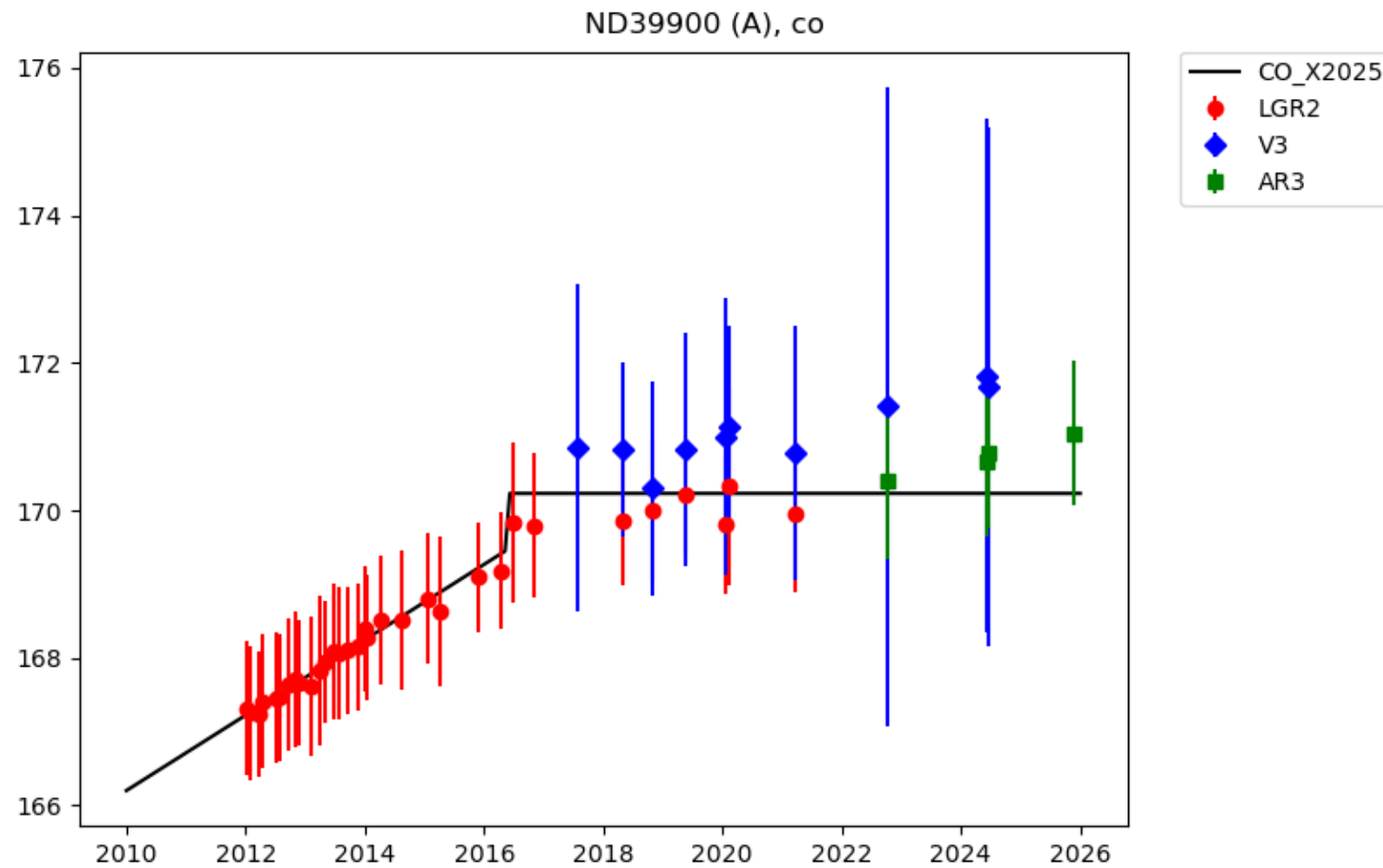
Current secondary standards – all data used for value assignments are calibrations verses the 2011 primary standards.



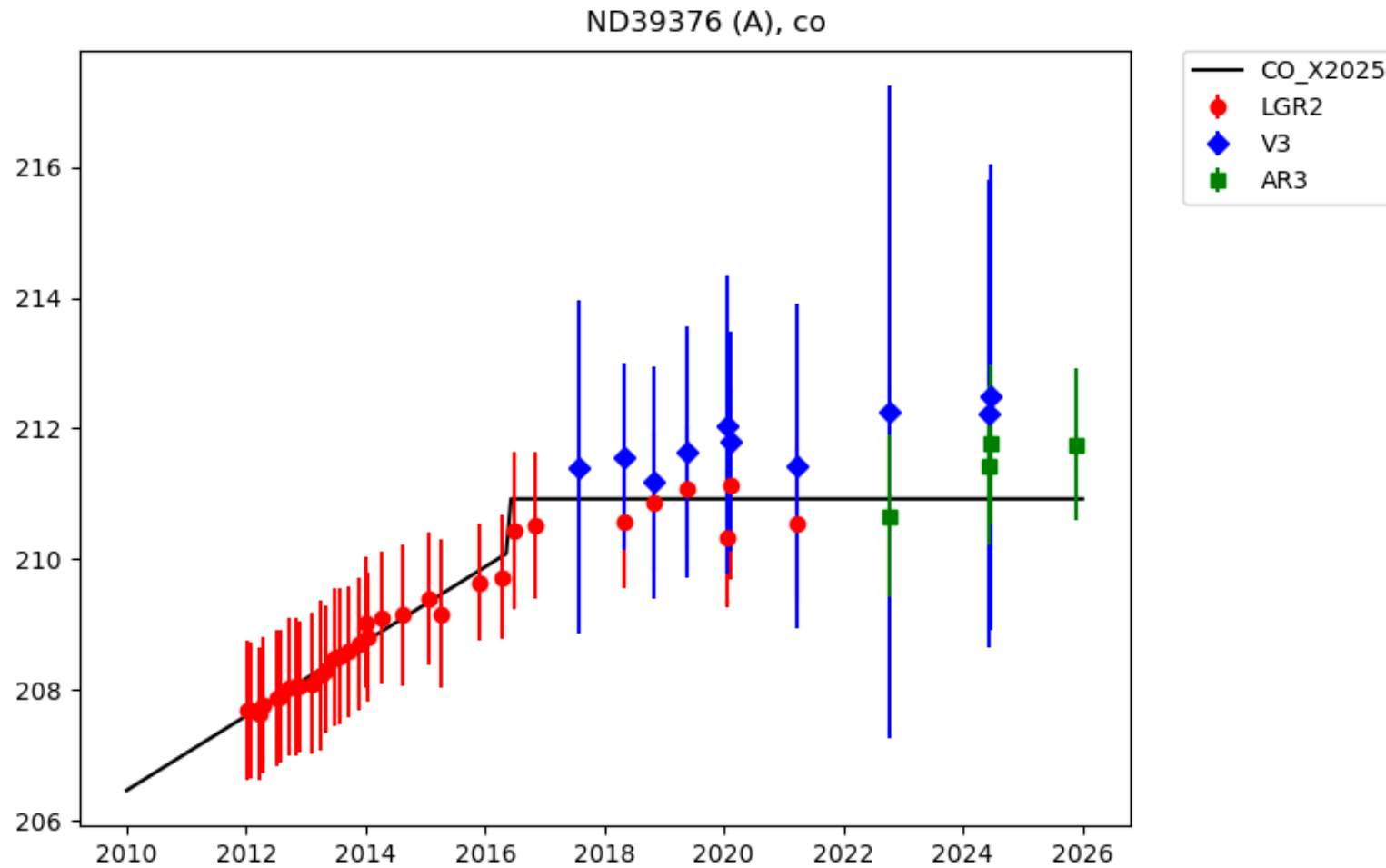
Current secondary standards – all data used for value assignments are calibrations versus the 2011 primary standards.



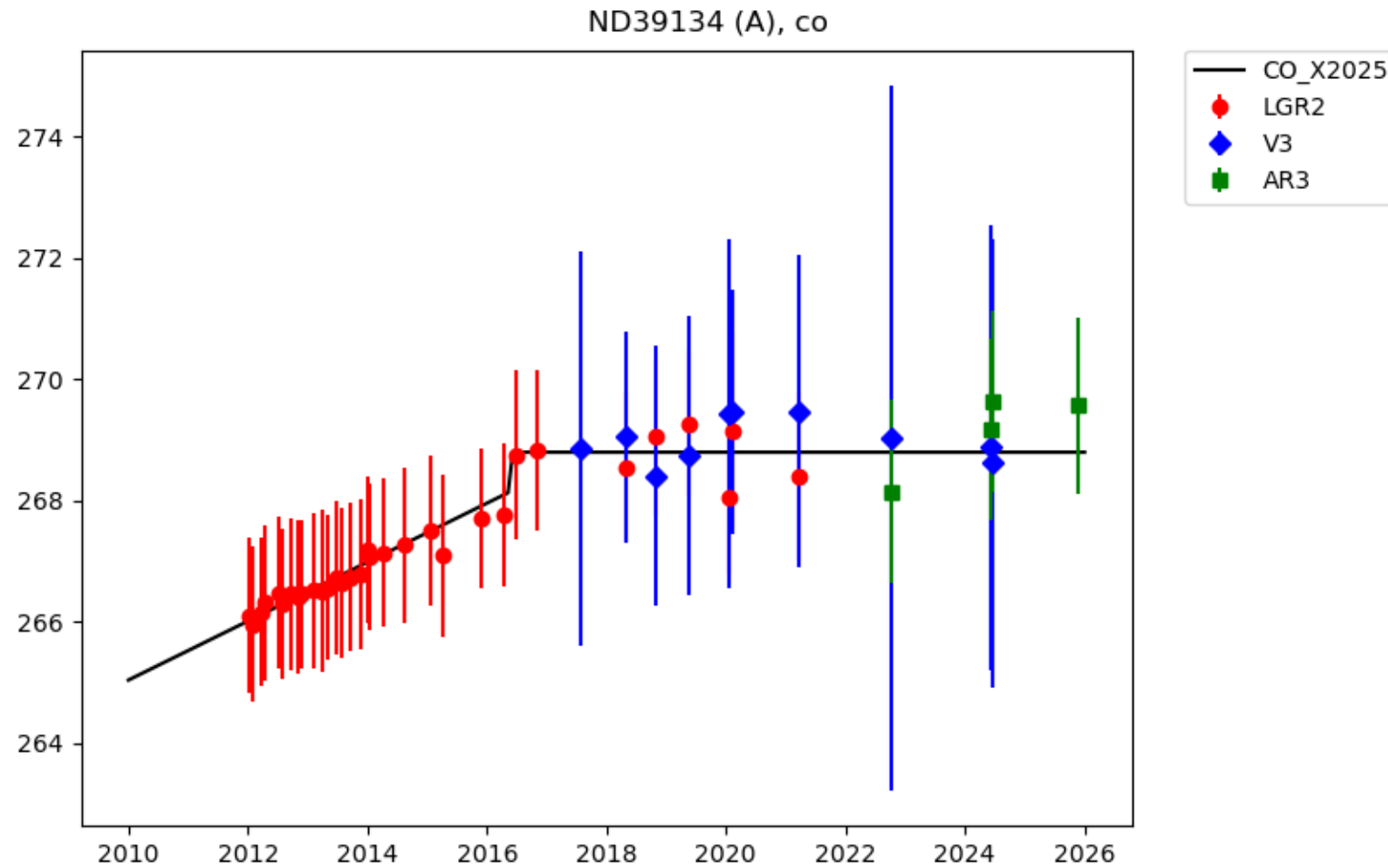
Current secondary standards – all data used for value assignments are calibrations verses the 2011 primary standards.



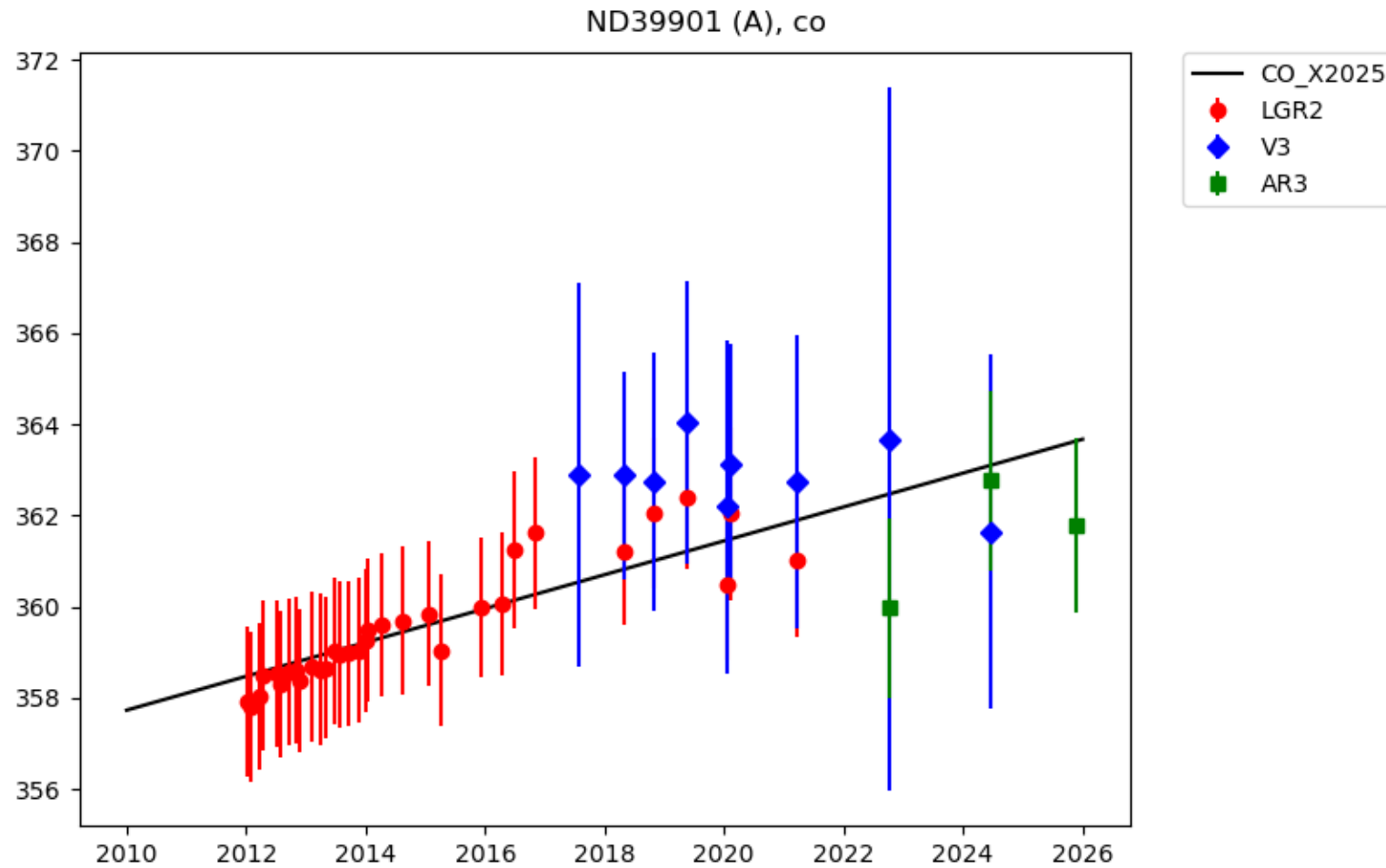
Current secondary standards – all data used for value assignments are calibrations versus the 2011 primary standards.



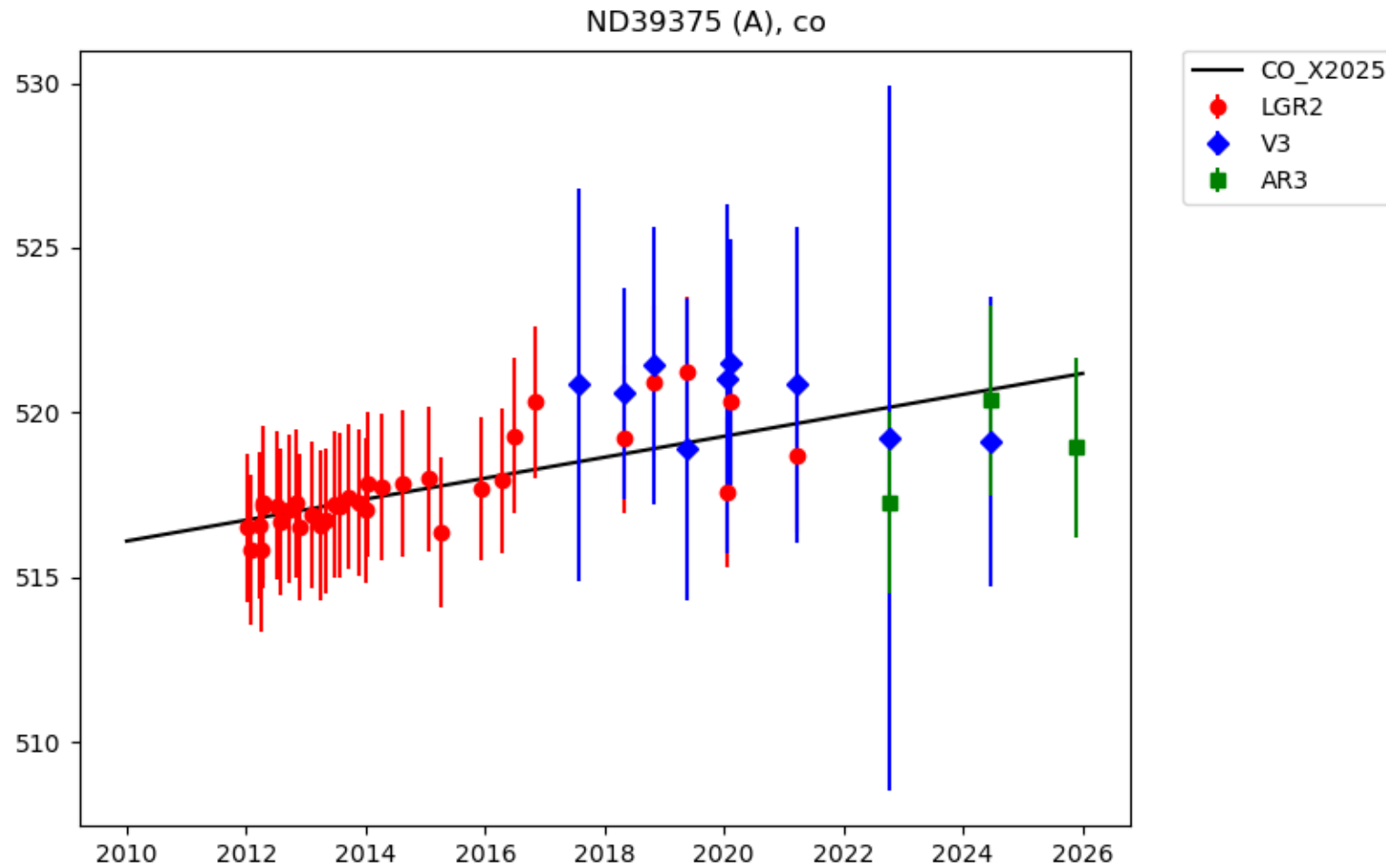
Current secondary standards – all data used for value assignments are calibrations versus the 2011 primary standards.



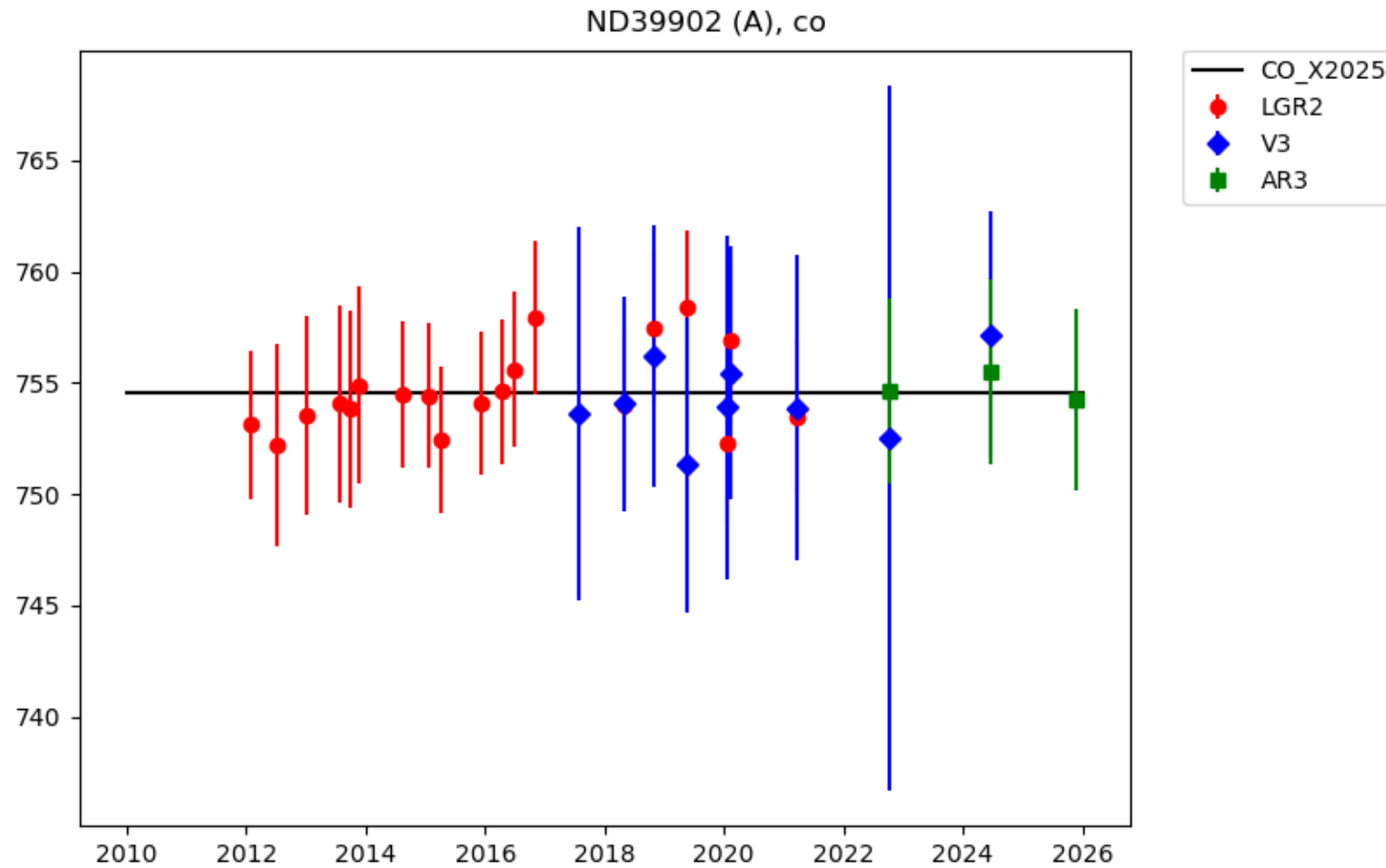
Current secondary standards – all data used for value assignments are calibrations versus the 2011 primary standards.



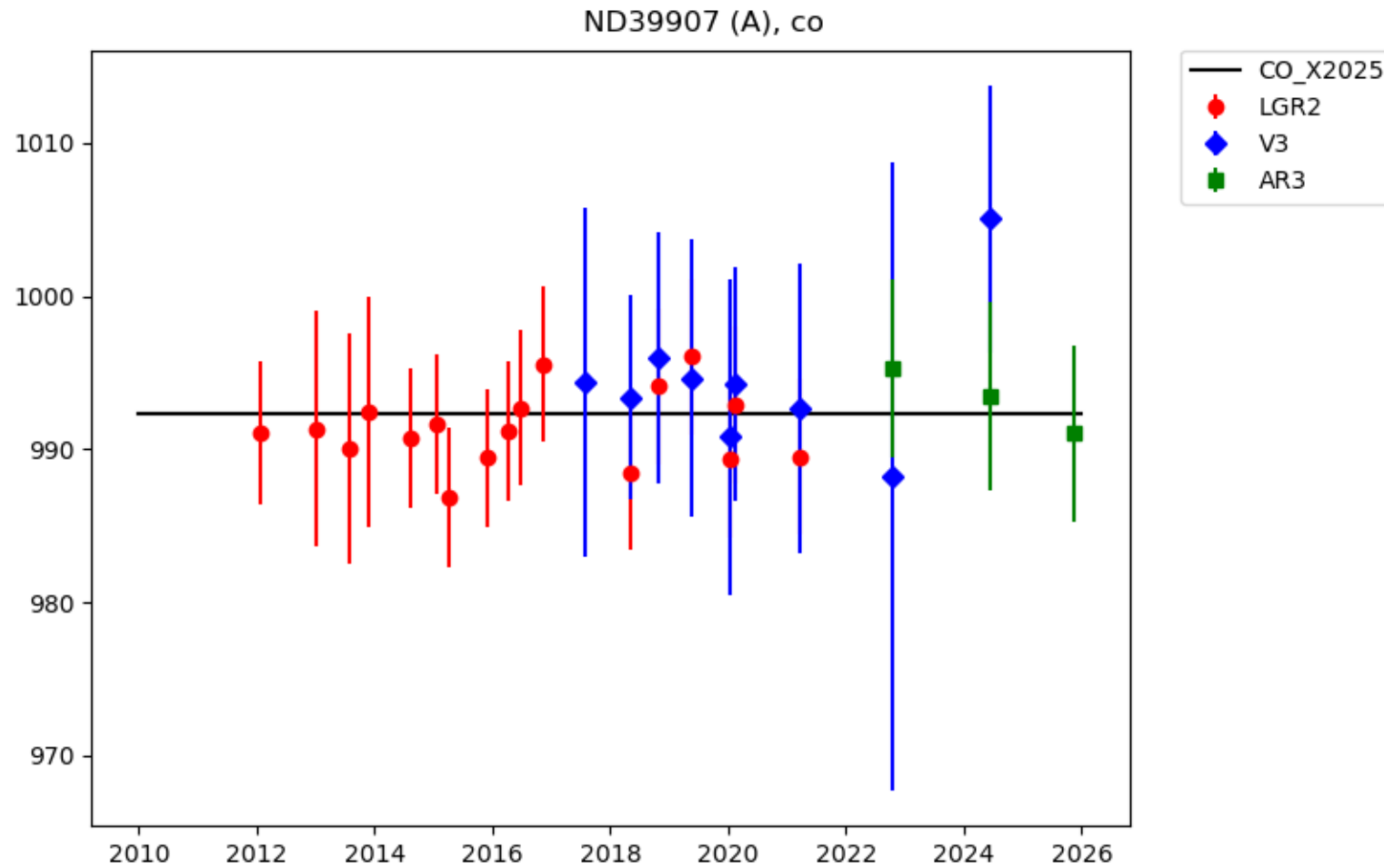
Current secondary standards – all data used for value assignments are calibrations versus the 2011 primary standards.



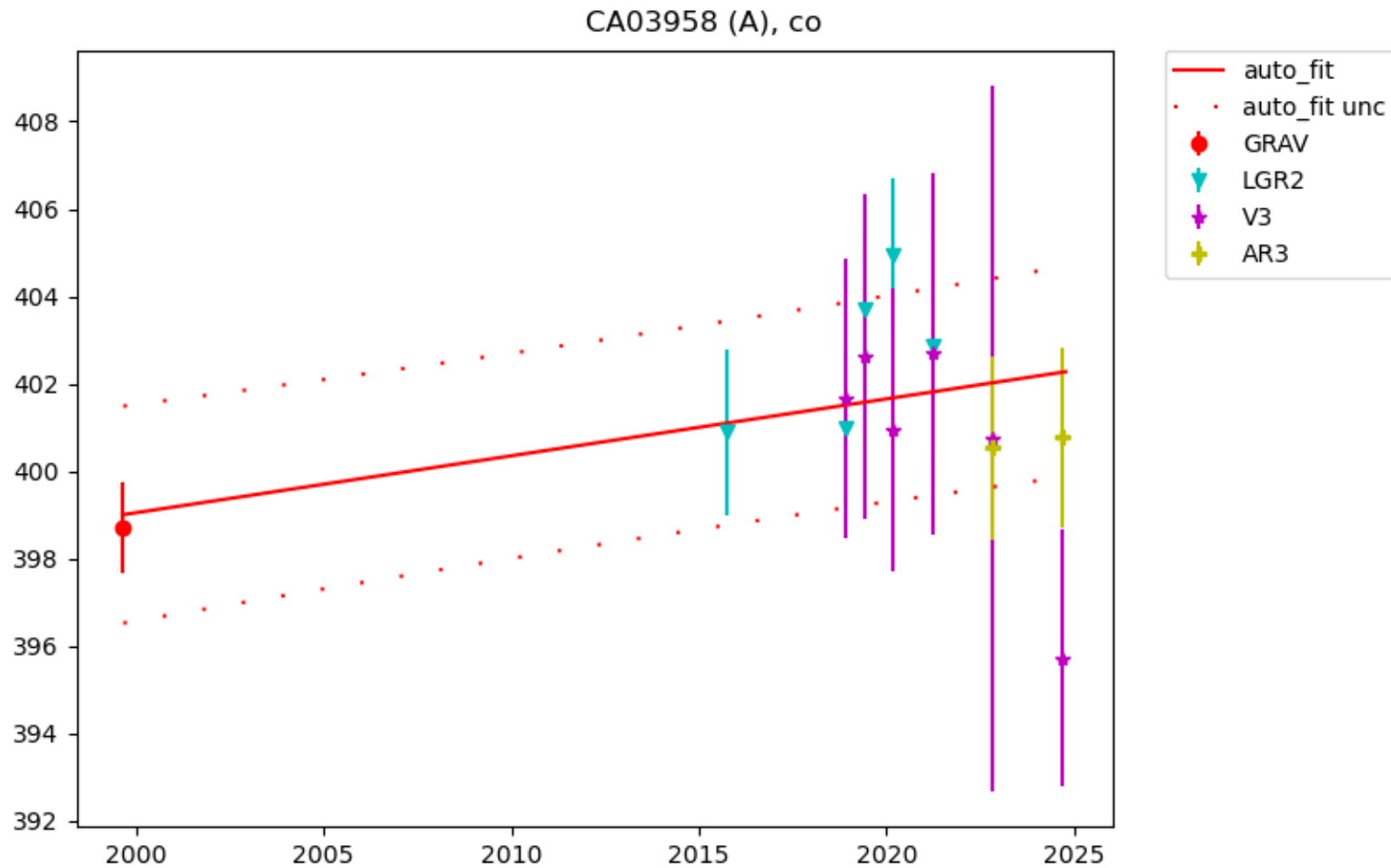
Current secondary standards – all data used for value assignments are calibrations versus the 2011 primary standards.



Current secondary standards – all data used for value assignments are calibrations versus the 2011 primary standards.

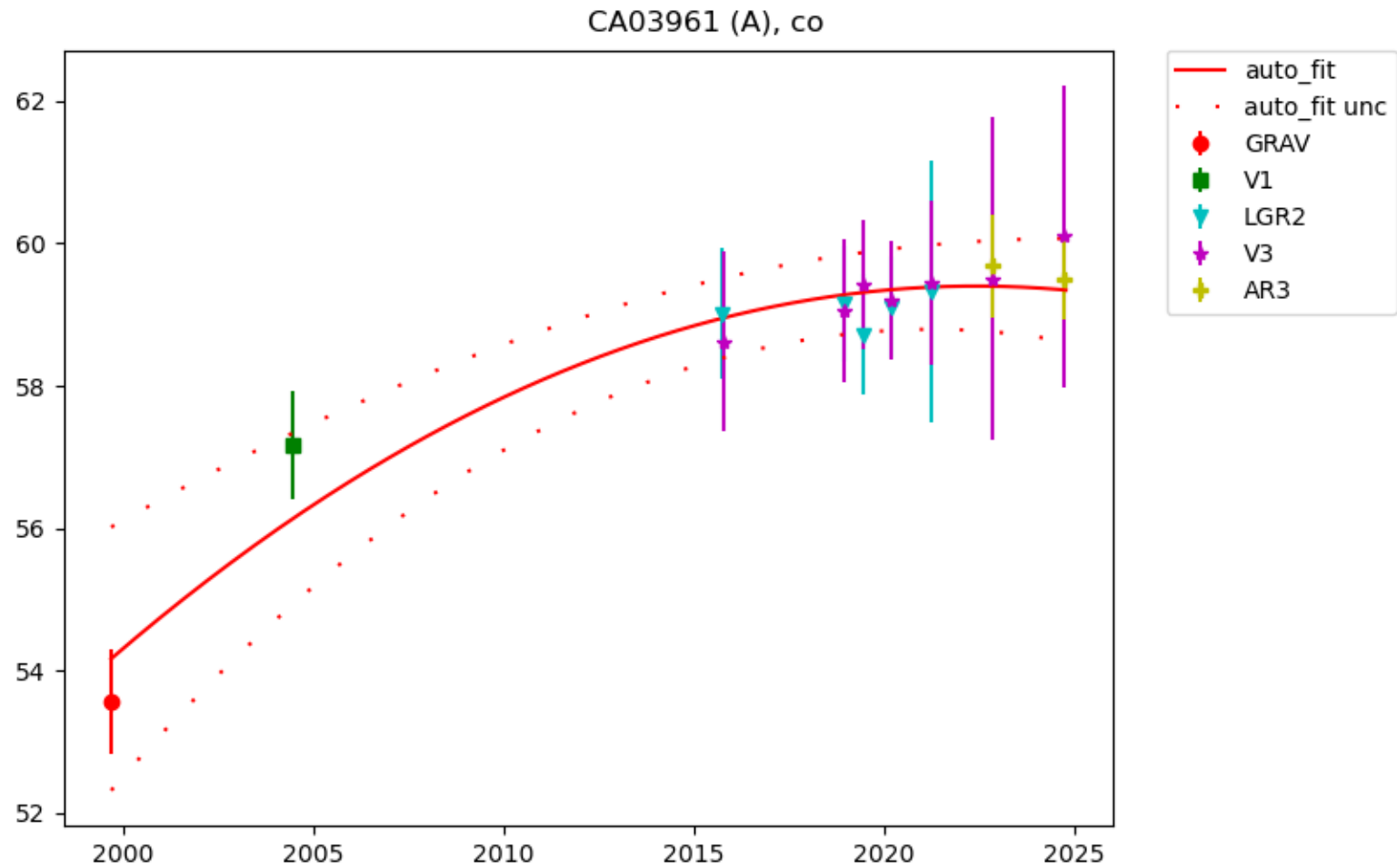


1999/2000 gravimetric standards



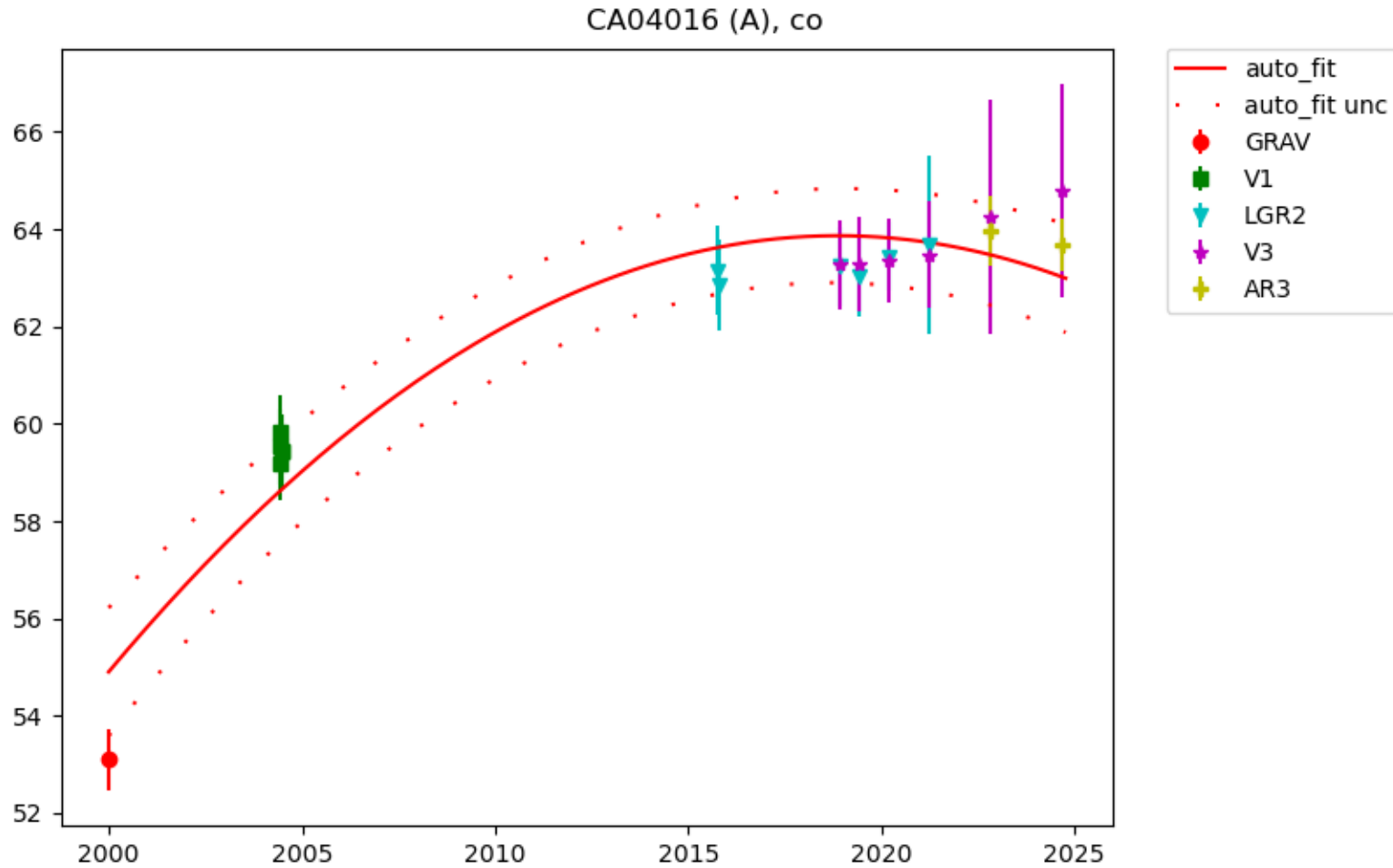
We assume this 1999/2000 gravimetric standard is reasonably stable over time as shown by agreement of gravimetric value with measurements vs dilution standards. Use this standard to help constrain drift observed in other members of the 1999/2000 gravimetric set.

1999/2000 gravimetric standards



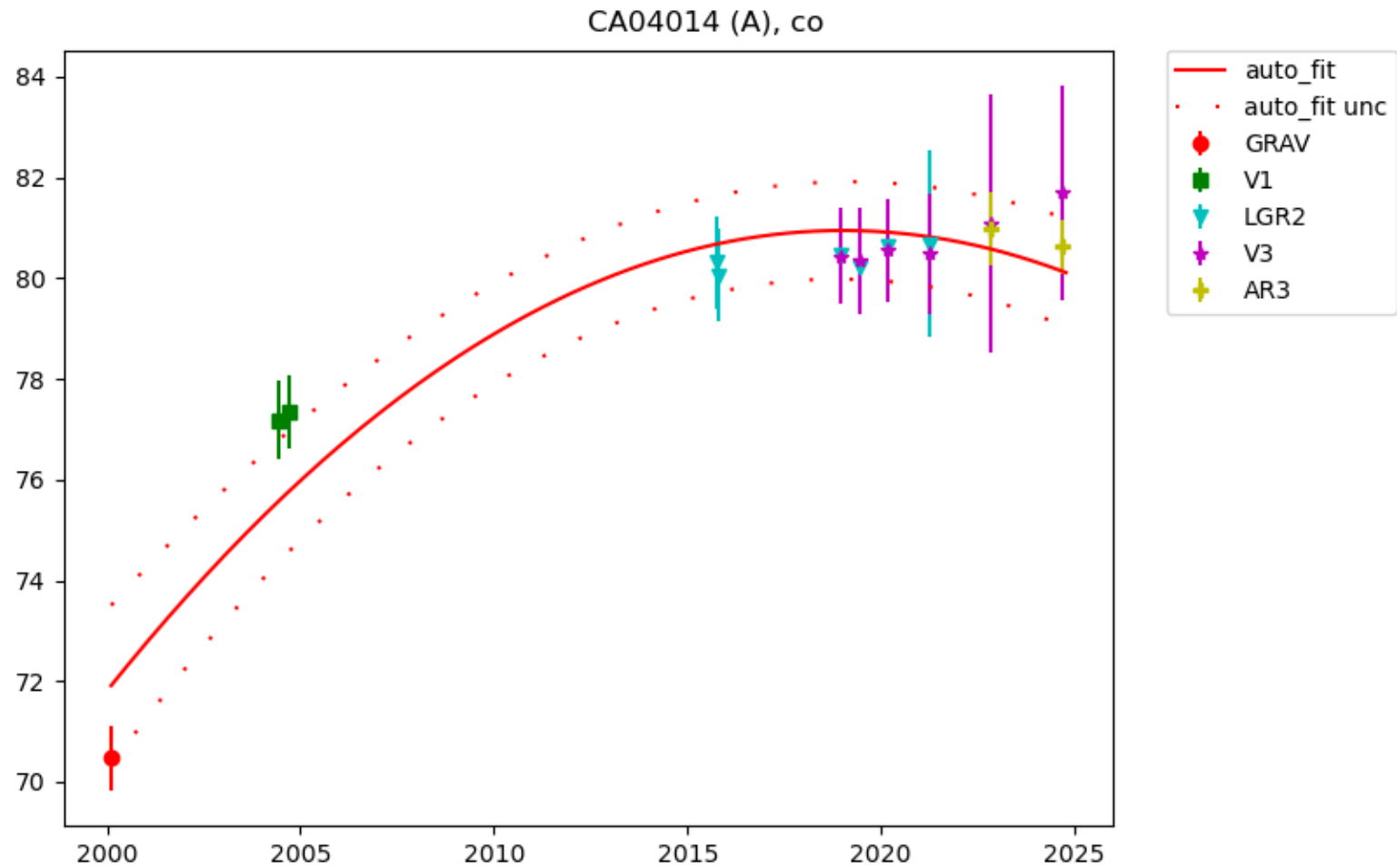
Value assignment based on gravimetric value, measurements vs dilution standards, and V1 measurement vs CA03958 (stable 400 ppb 1999 grav).

1999/2000 gravimetric standards



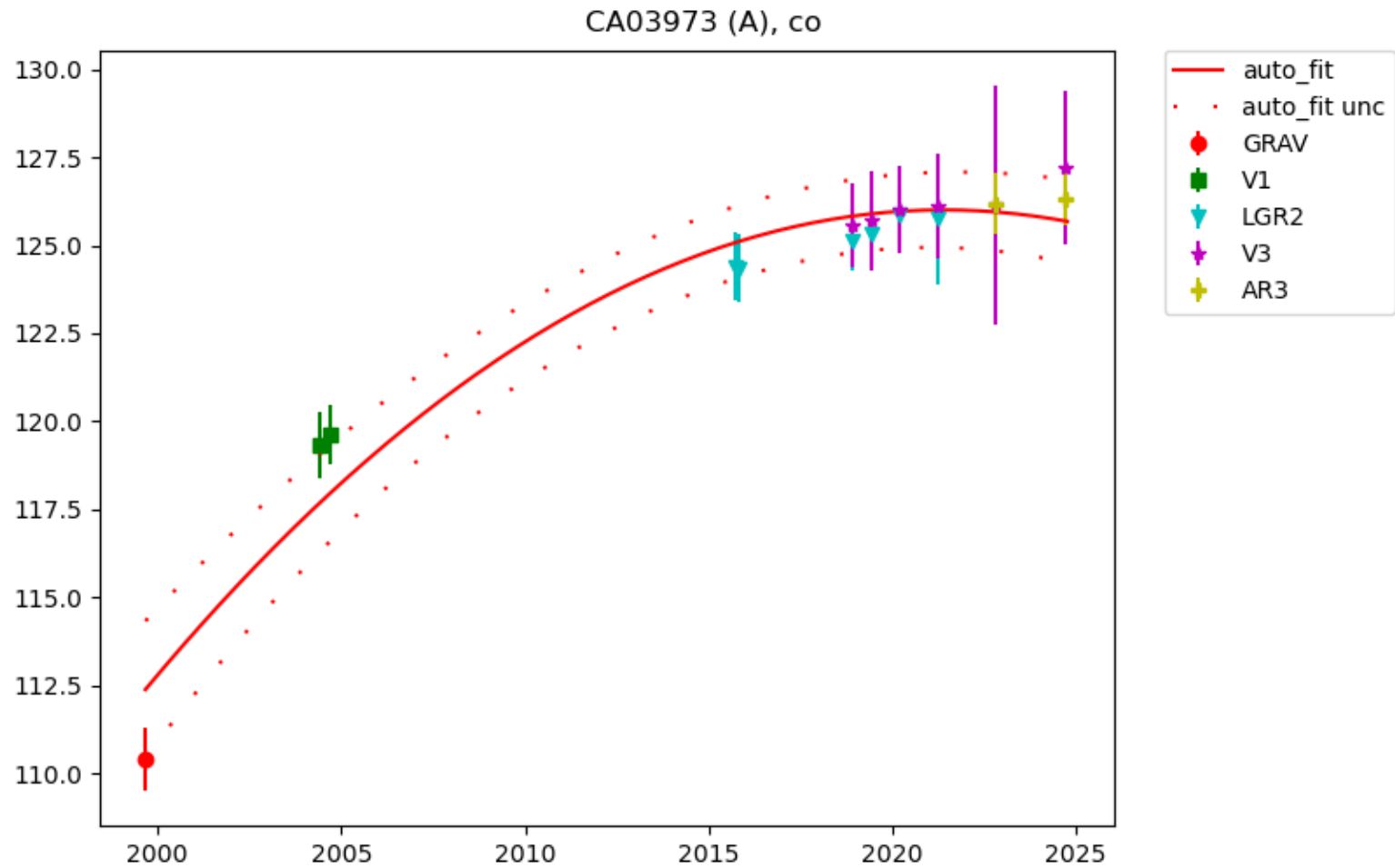
Value assignment based on gravimetric value, measurements vs dilution standards, and V1 measurement vs CA03958 (stable 400 ppb 1999 grav).

1999/2000 gravimetric standards



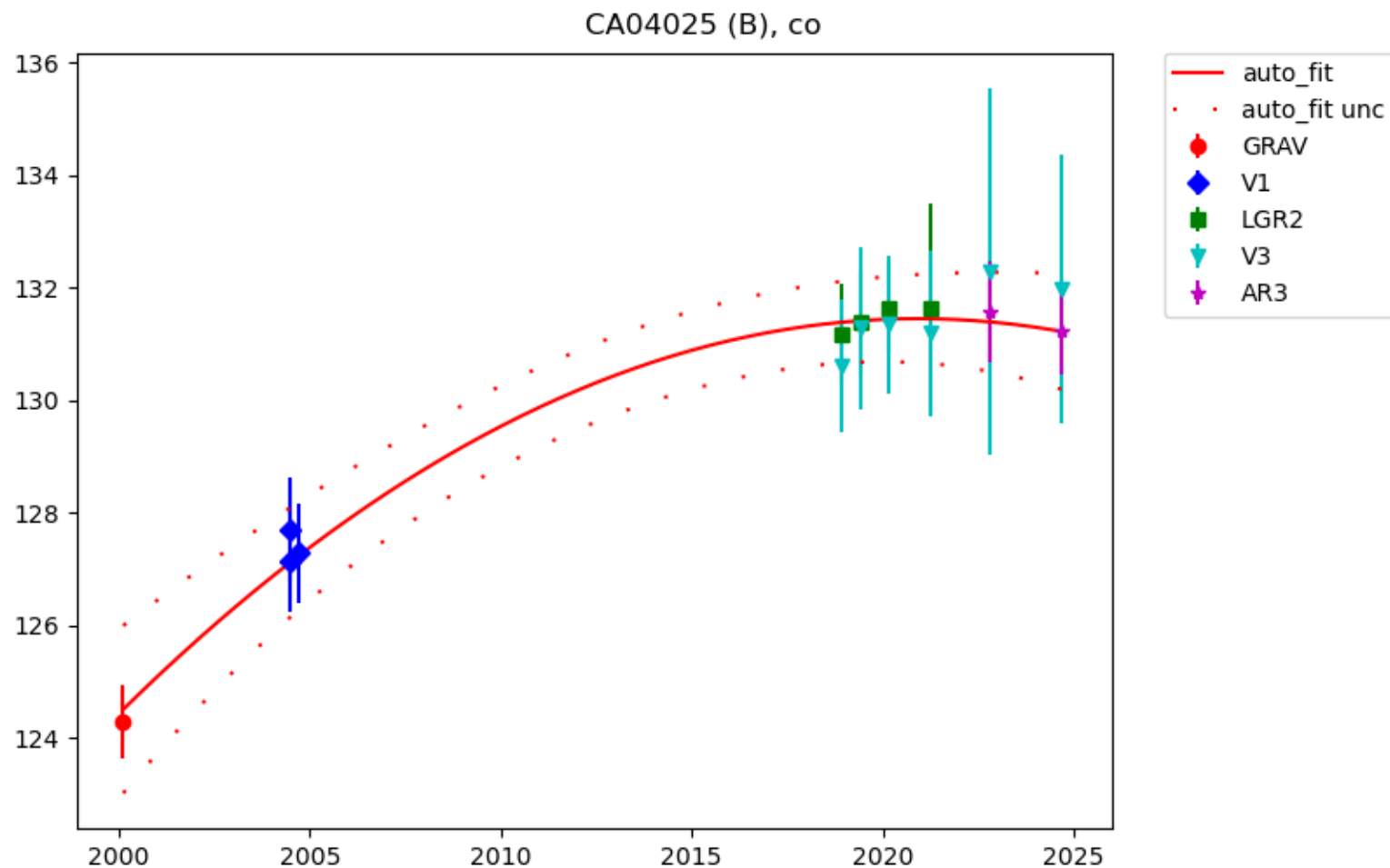
Value assignment based on gravimetric value, measurements vs dilution standards, and V1 measurement vs CA03958 (stable 400 ppb 1999 grav).

1999/2000 gravimetric standards



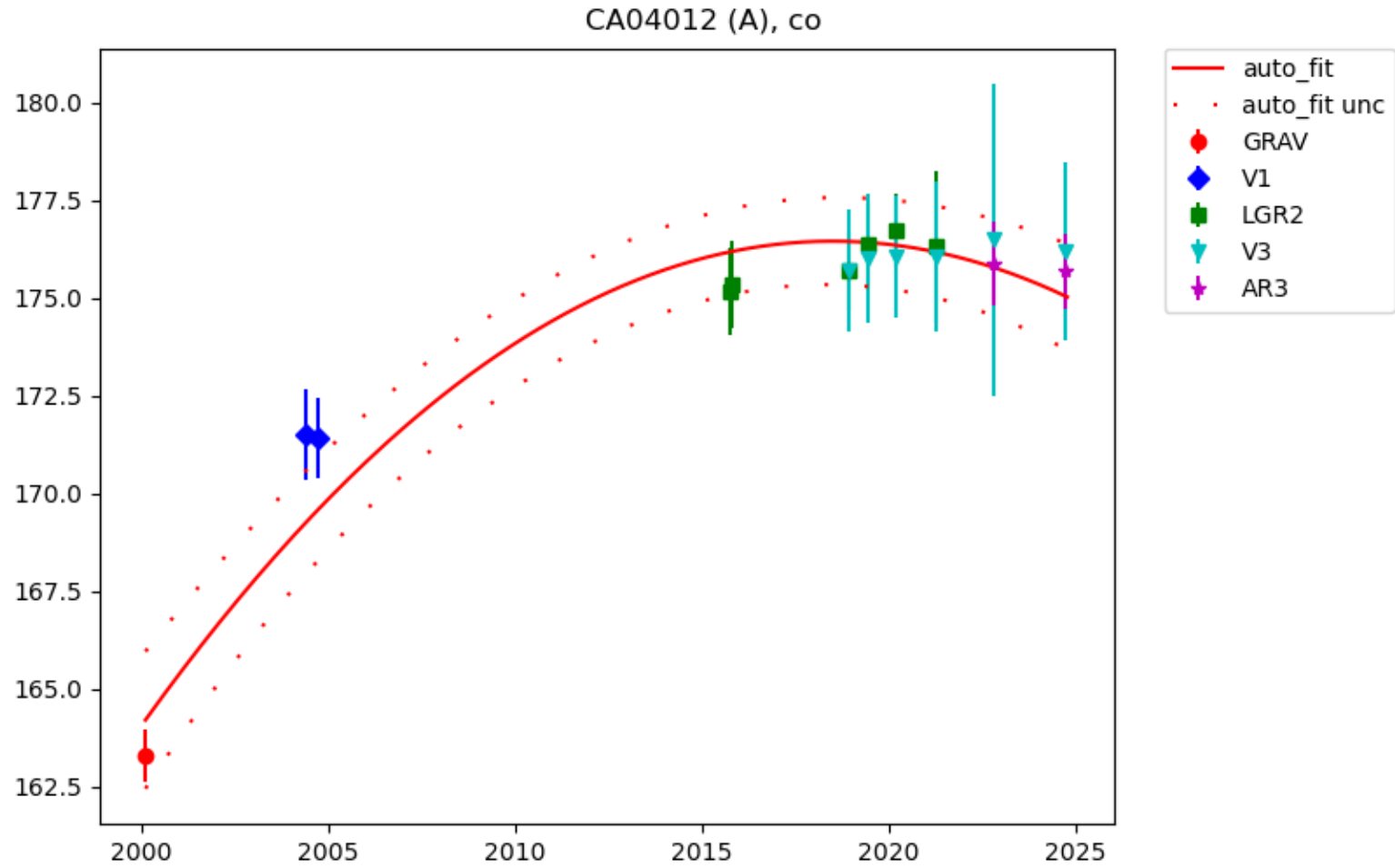
Value assignment based on gravimetric value, measurements vs dilution standards, and V1 measurement vs CA03958 (stable 400 ppb 1999 grav).

1999/2000 gravimetric standards



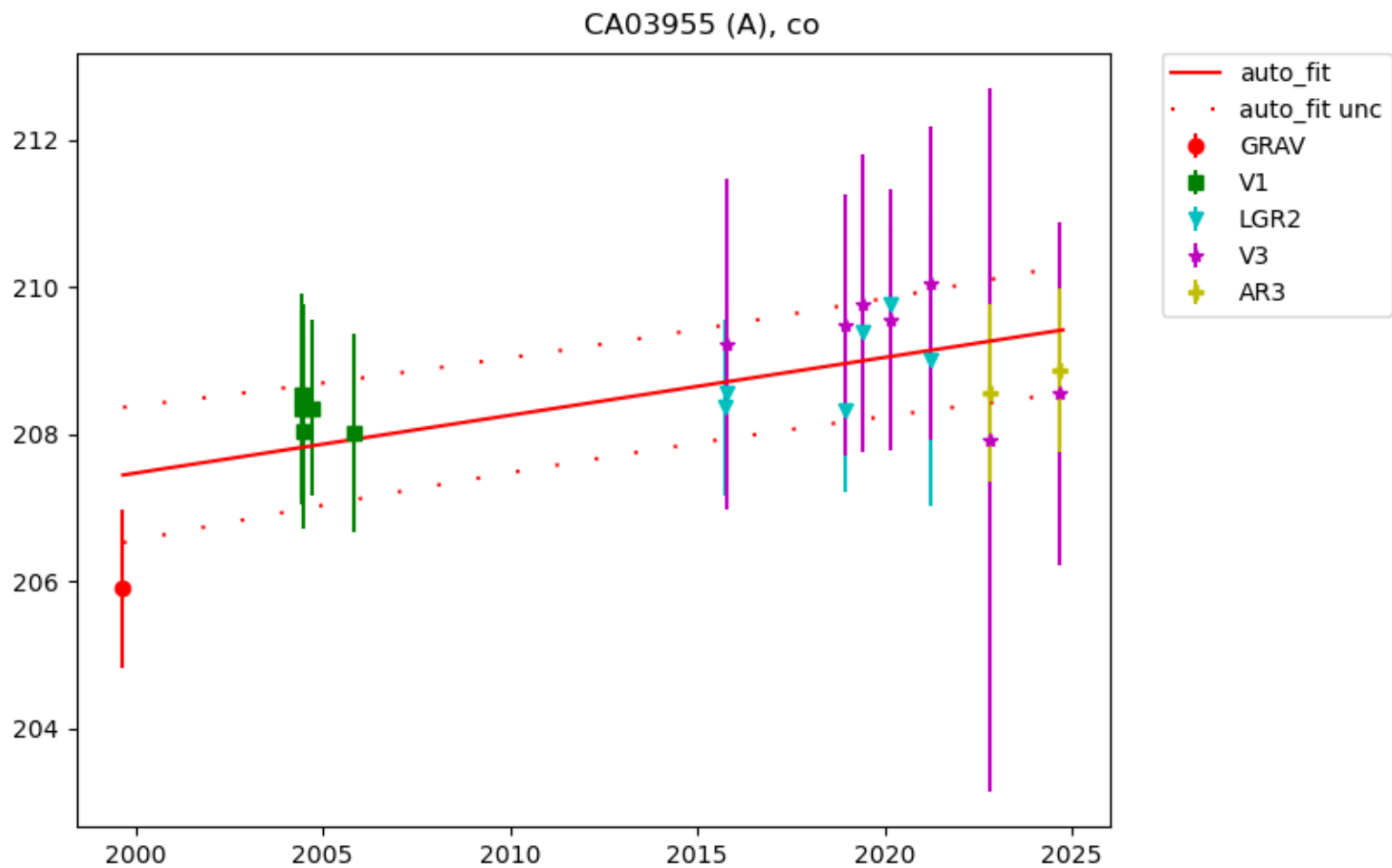
Value assignment based on gravimetric value, measurements vs dilution standards, and V1 measurement vs CA03958 (stable 400 ppb 1999 grav).

1999/2000 gravimetric standards



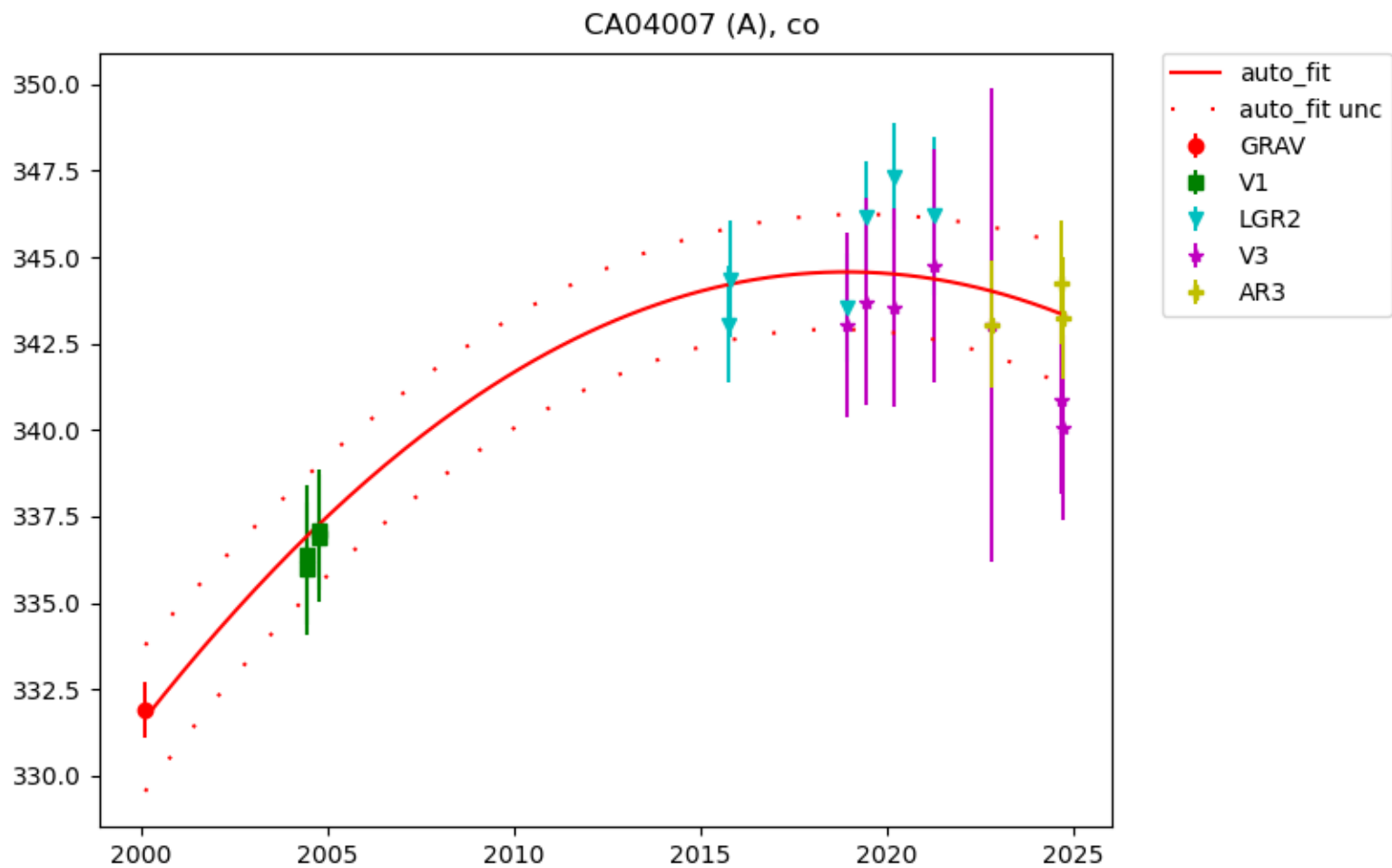
Value assignment based on gravimetric value, measurements vs dilution standards, and V1 measurement vs CA03958 (stable 400 ppb 1999 grav).

1999/2000 gravimetric standards



Value assignment based on gravimetric value, measurements vs dilution standards, and V1 measurement vs CA03958 (stable 400 ppb 1999 grav).

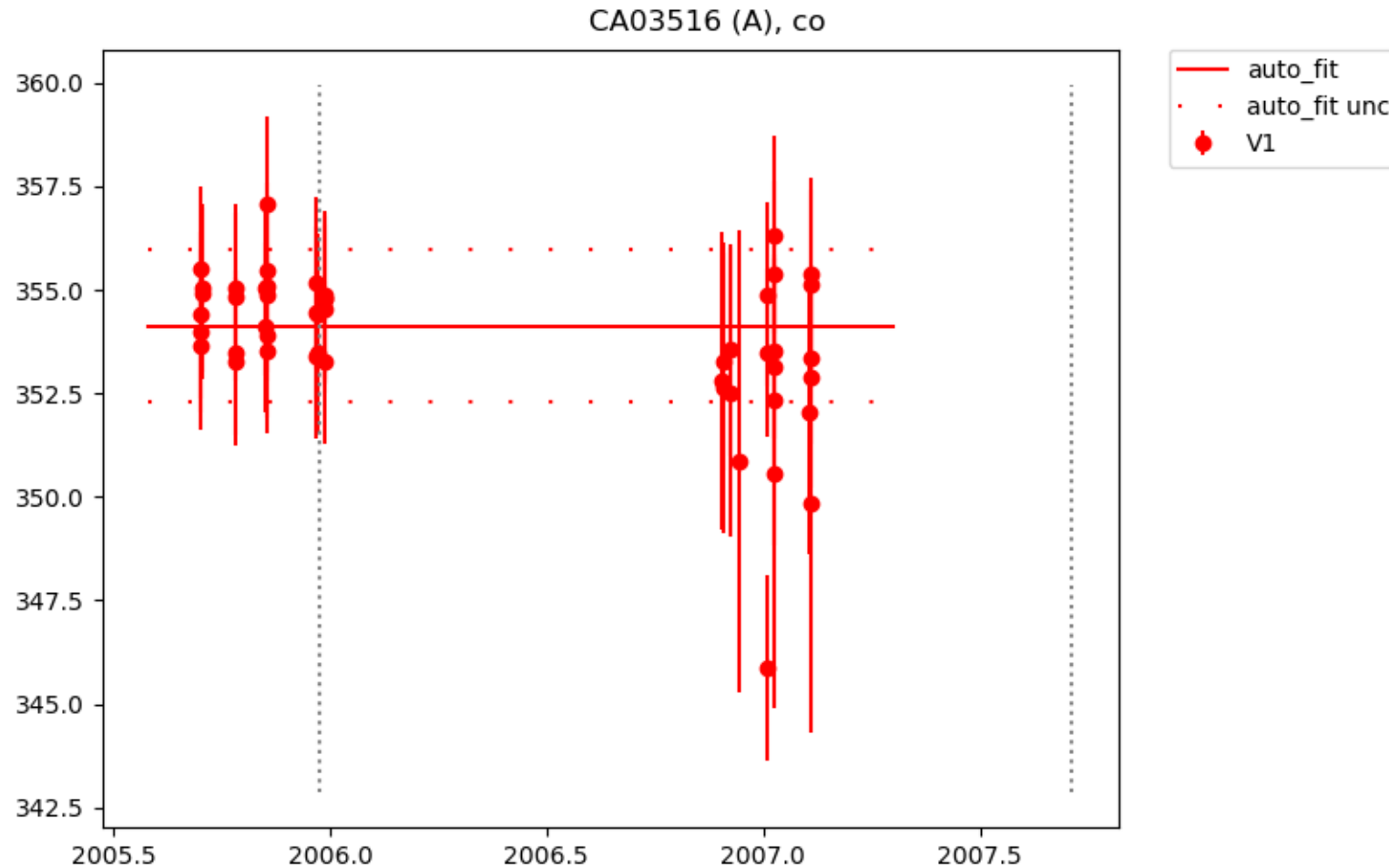
1999/2000 gravimetric standards



Value assignment based on gravimetric value, measurements vs dilution standards, and V1 measurement vs CA03958 (stable 400 ppb 1999 grav).

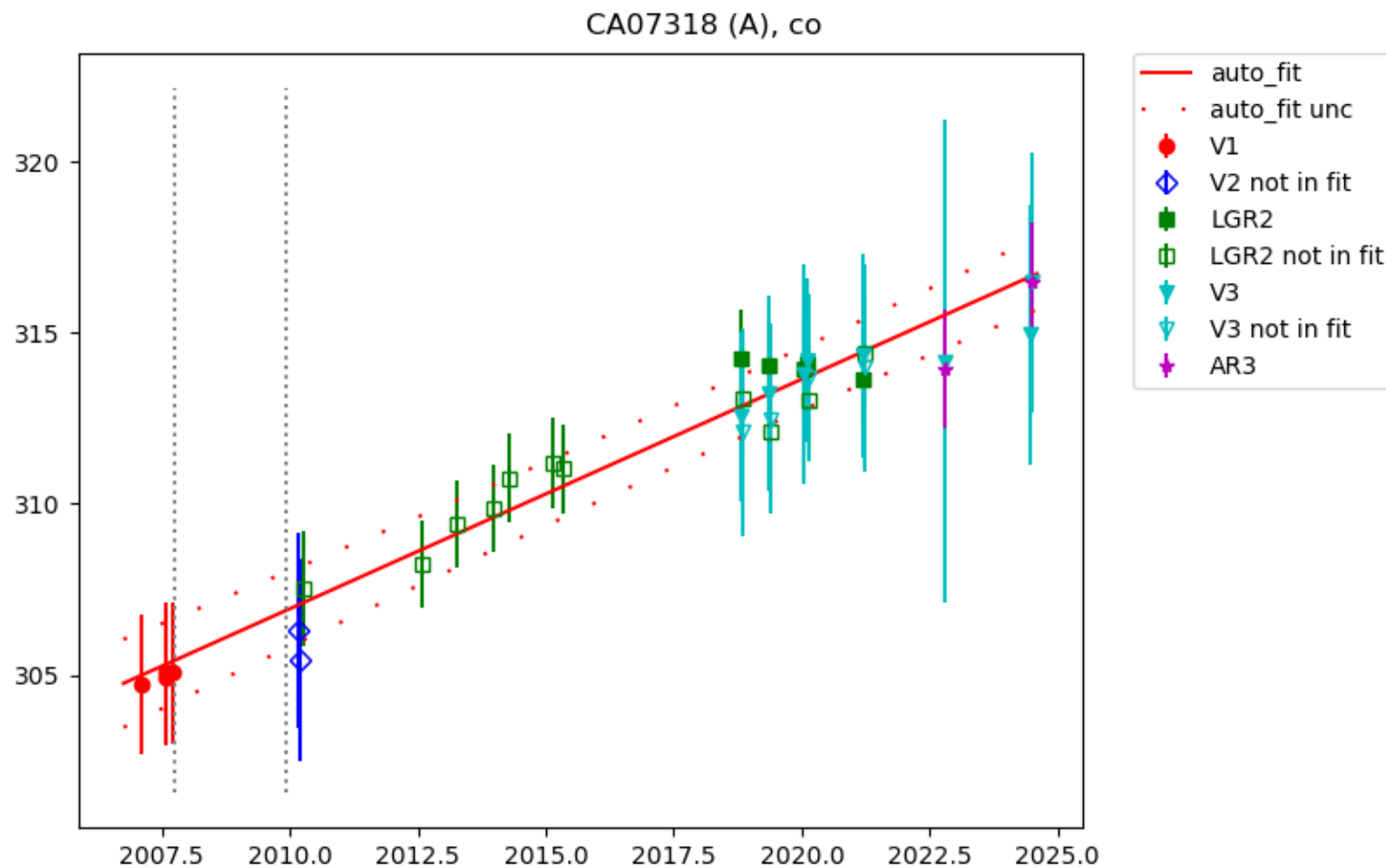
V1 secondary standards

CA03516 used as a secondary standard on V1, in use 2005-12-23, 2007-09-18 shown by vertical dashed lines. Pre-deployment calibrations vs CA03958 and CA04007. Mid-deployment calibrations vs individual members of the 2006 gravimetric standard set.



V1 secondary standards

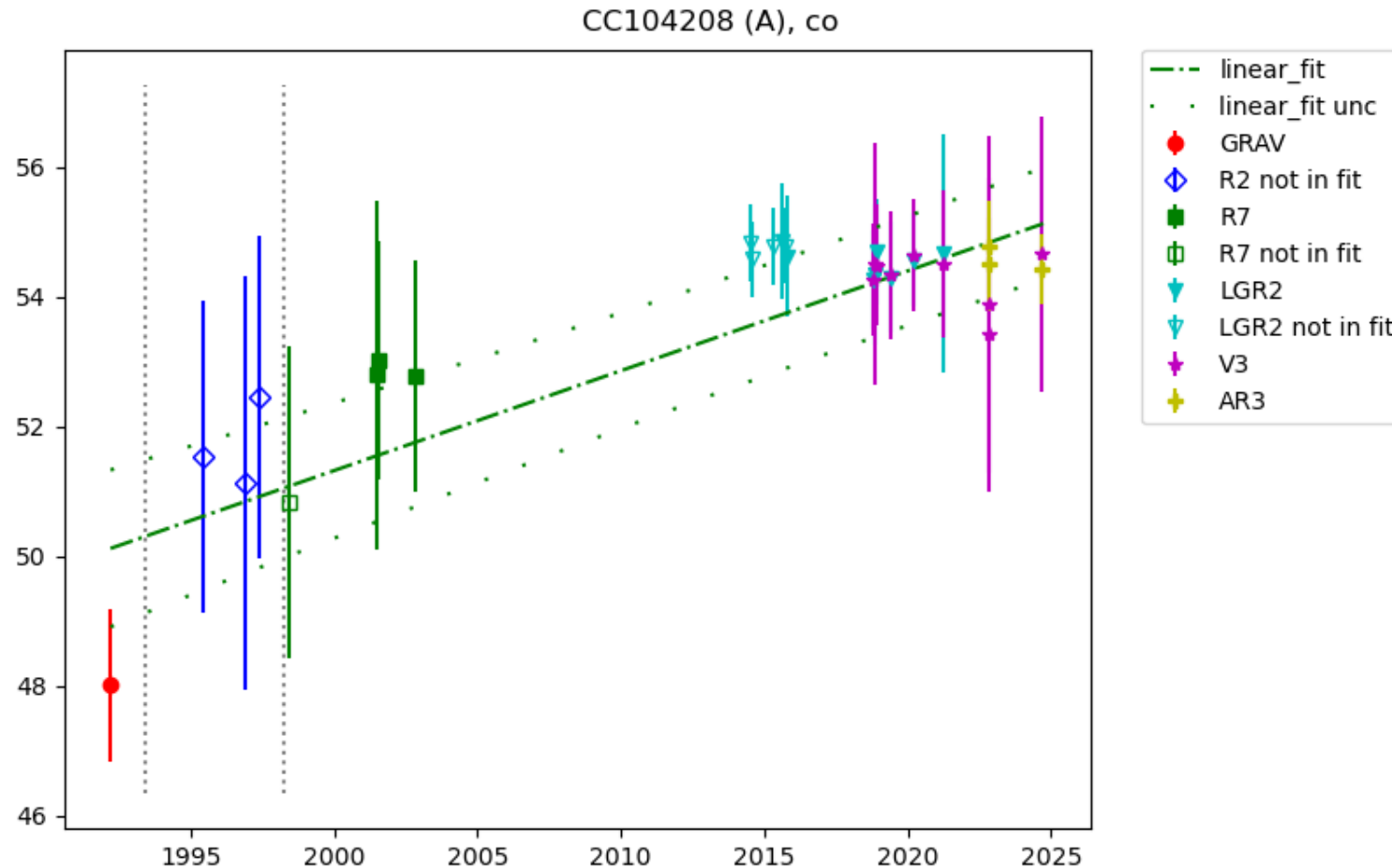
CA07318 used as a secondary standard on V1, in use 2007-09-27 through 2009-12-03. Value assignment based on pre-deployment measurements vs prior V1 secondary standard CA03516 and post deployment measurements vs the 2011 primary standards. Vertical bars show the in-service time for this standard. Measurement results shown in open symbols are vs other secondary standards. These are not used in the value assignment but do indicate the linear rate of CO growth is likely.



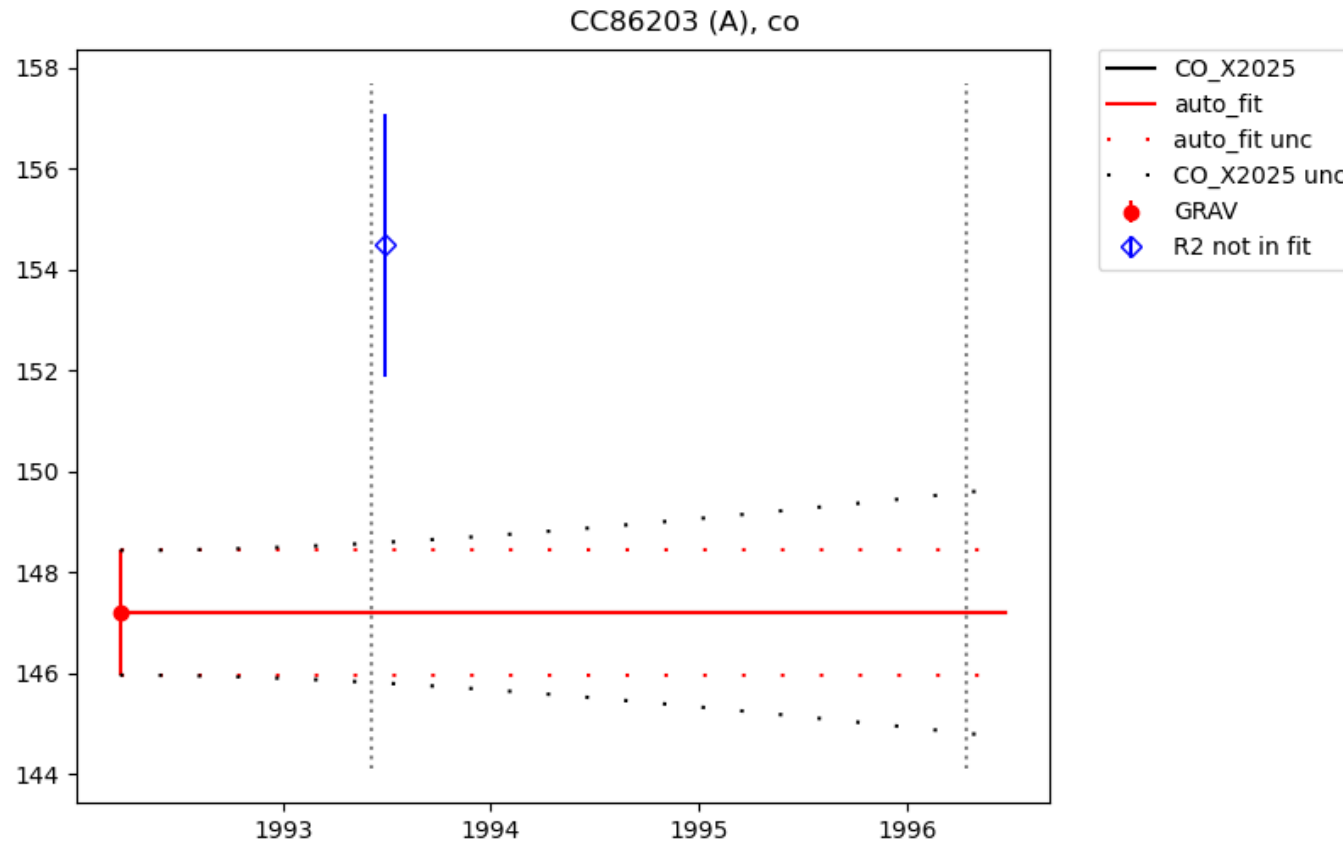
Secondary standards used on RGD2 system during 1990s

This was one of the 1992 gravimetric standards. Filled symbols indicate independent measurements traceable to the scale. Open symbols indicate measurements relative to other secondary standards that may not be independent. These were not used to value assign the standards since they are not independent. However, they do help to show consistency across time.

Using Linear fit based on looking at residuals of calibration curves using this standard. Vertical dashed line show time period this standard was in service (1993-06-04 – 1998-03-27).

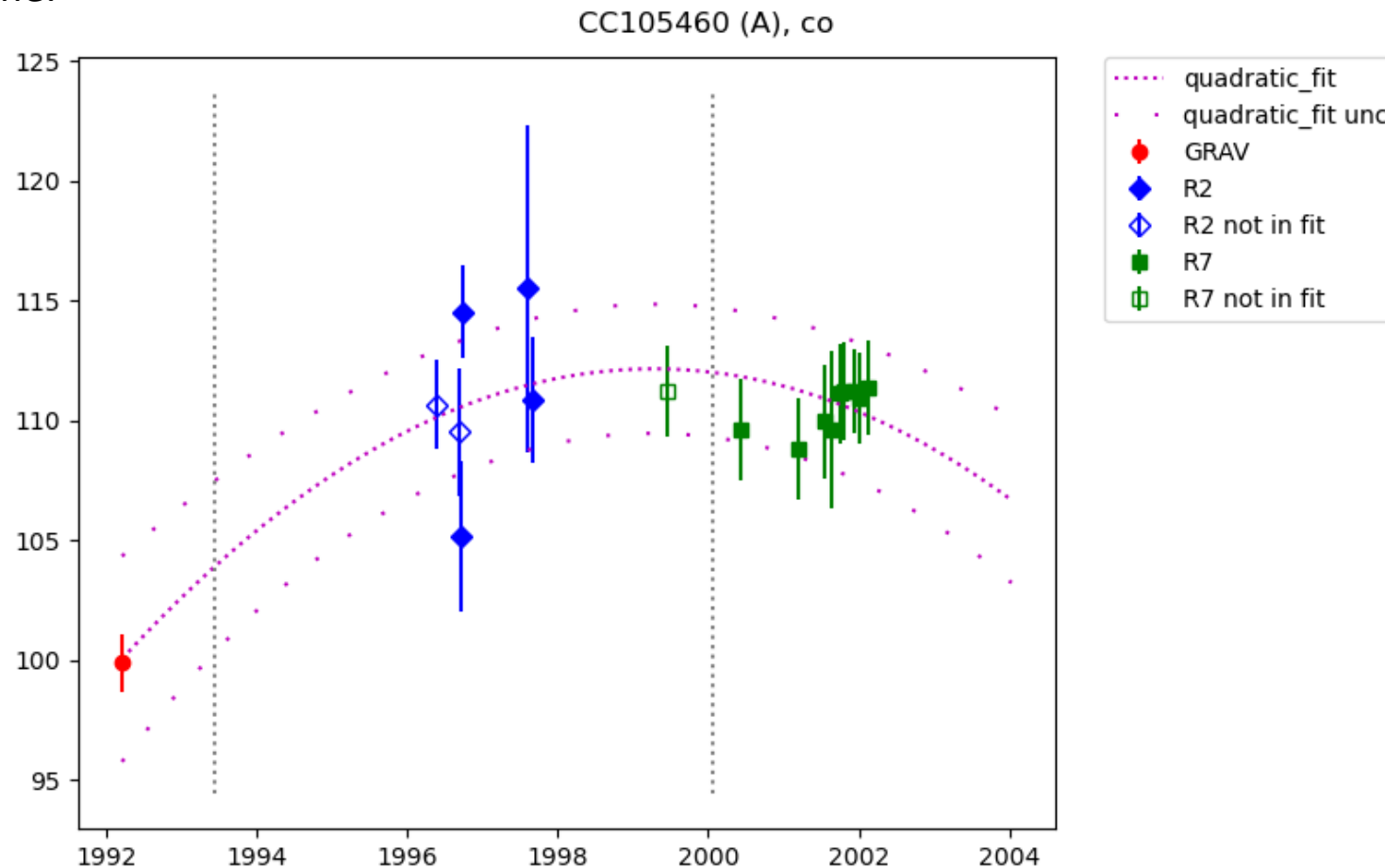


Secondary standards used on RGD2 system during 1990s
CC86203 was a 1992 gravimetric standard. Filled symbols indicate independent measurements traceable to the scale. Open symbols indicate measurements relative to other secondary standards that may not be independent. These were not used to value assign the standards since they are not independent. Vertical dashed line show time period this standard was in service (1993-06-04 – 1996-04-15).
Time dependent uncertainty term of 0.5 ppb per year added to value assignment of CC86203 since no other measurements made. We do not know why this tank was never remeasured. Could have been accidentally drained at some point prior to new grav's being made.



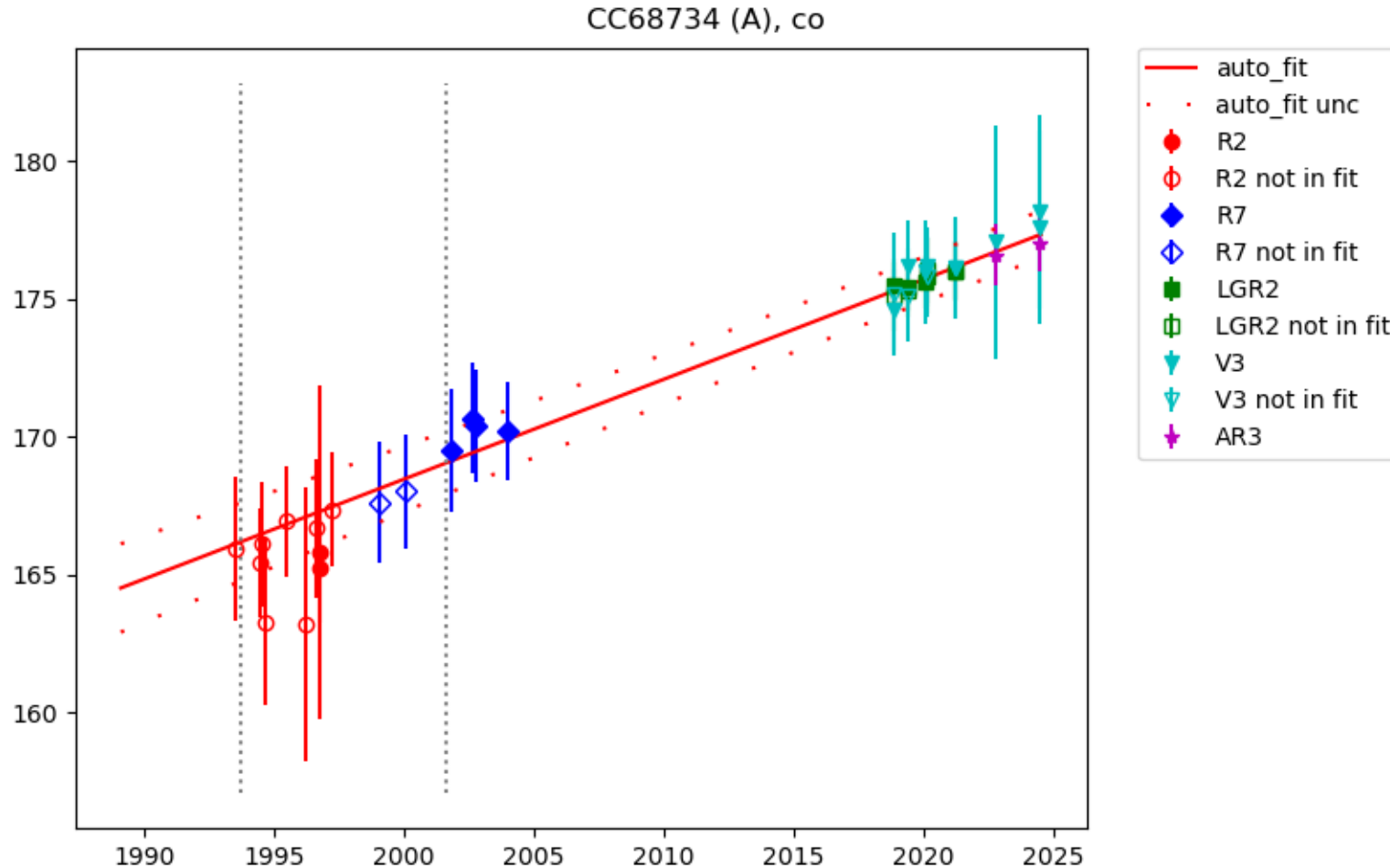
Secondary standards used on RGD2 system during 1990s
CC105460 was a 1992 gravimetric standard. Filled symbols indicate independent measurements traceable to the scale. Open symbols indicate measurements relative to other secondary standards. These were not used to value assign the standards since they are not independent. However, they do help to show consistency across time. Vertical dashed line show time period this standard was in service (1993-06-09 – 2000-01-26).

Using quadratic fit for this standard based on looking at residuals of calibration curves using this standard over time.



Secondary standards used on RGD2 system during 1990s

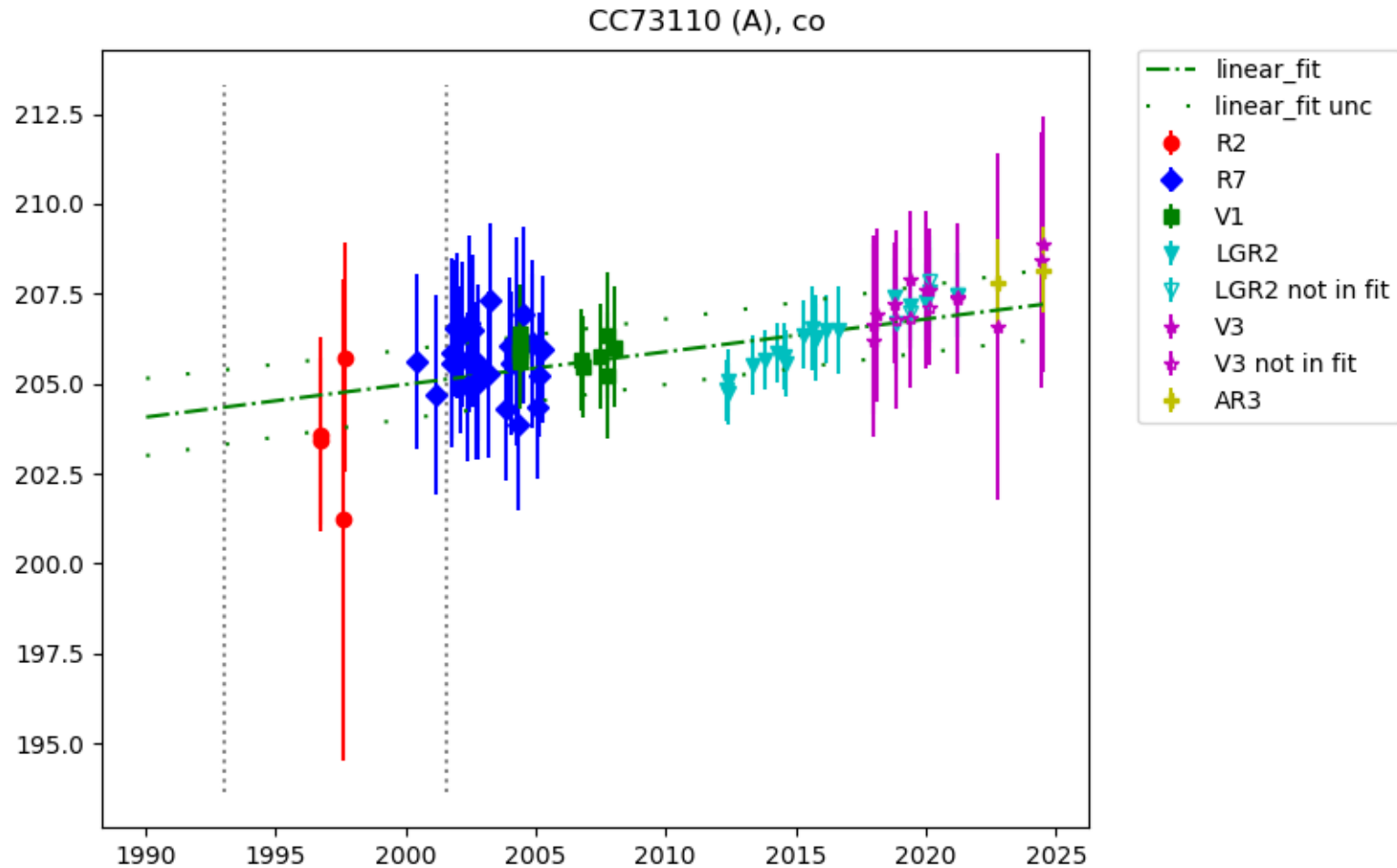
Filled symbols indicate independent measurements traceable to the scale. Open symbols indicate measurements relative to other secondary standards. These were not used to value assign the standards since they are not independent. However, they do help to show consistency across time. Vertical dashed line show time period this standard was in service.



Secondary standards used on RGD2 system during 1990s

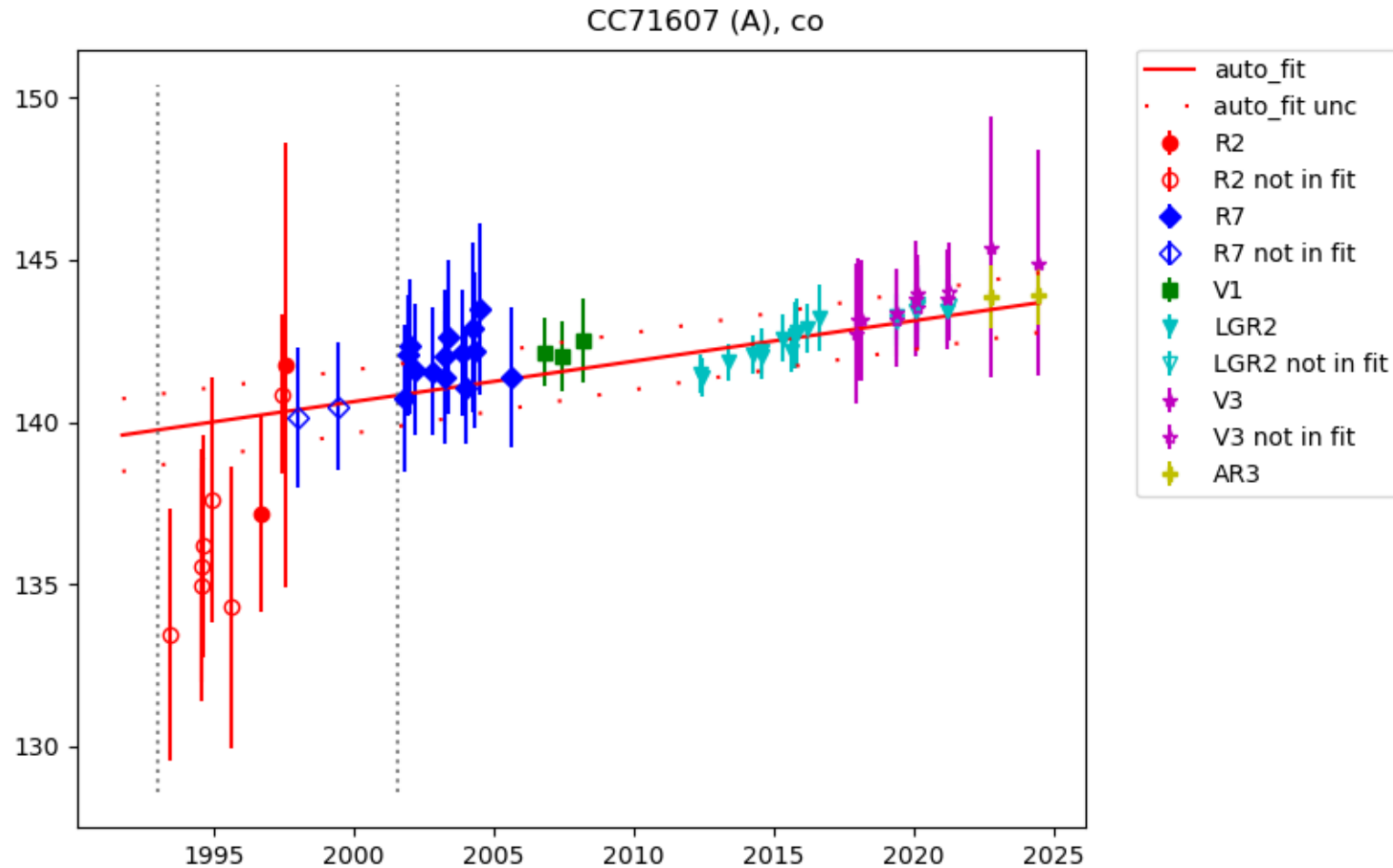
Filled symbols indicate independent measurements traceable to the scale. Open symbols indicate measurements relative to other secondary standards. These were not used to value assign the standards since they are not independent. However, they do help to show consistency across time. Vertical dashed line show time period this standard was in service (1993-01-07– 2001-8-09).

Force linear fit for this standard.



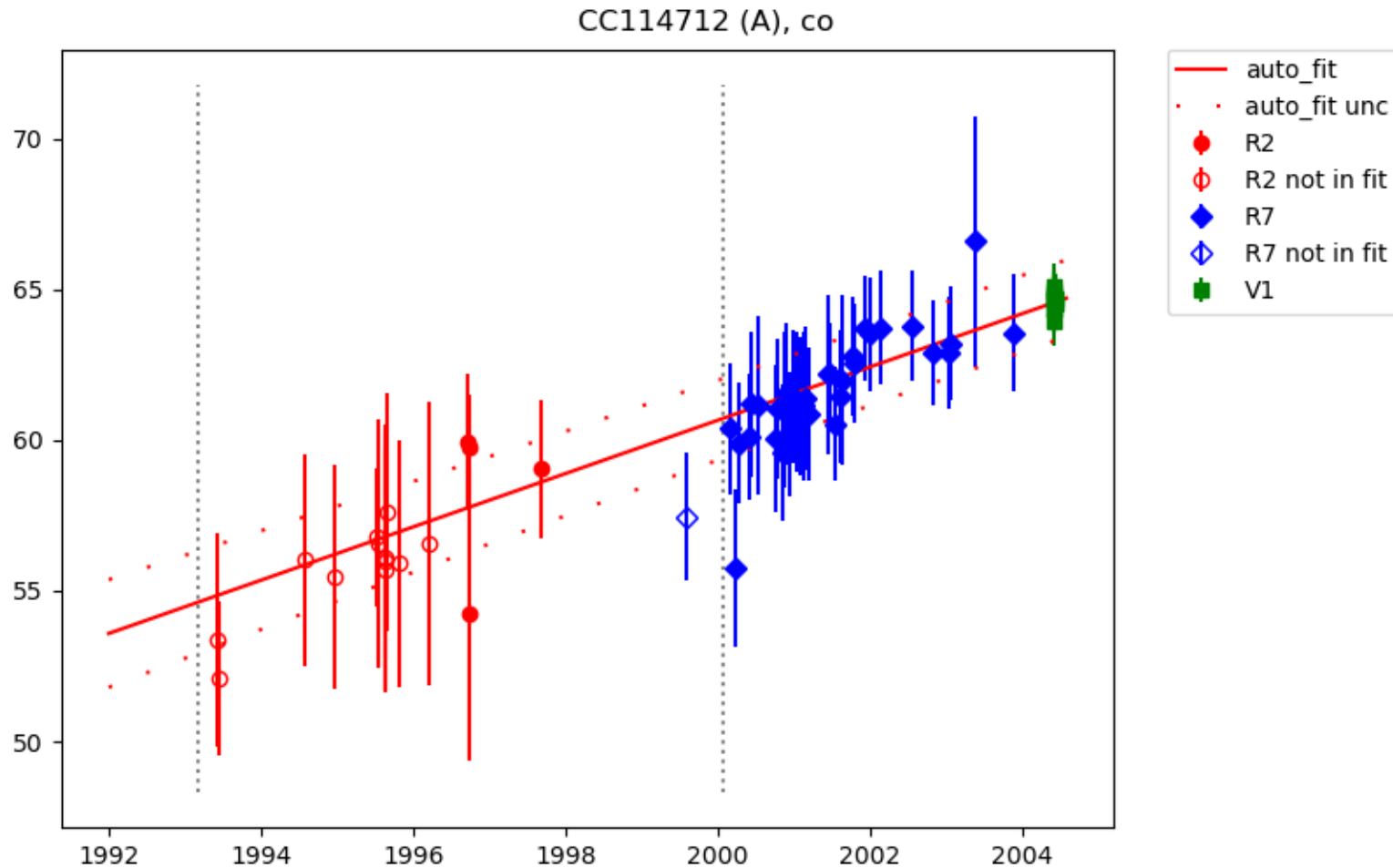
Secondary standards used on RGD2 system during 1990s

Filled symbols indicate independent measurements traceable to the scale. Open symbols indicate measurements relative to other secondary standards. These were not used to value assign the standards since they are not independent. However, they do help to show consistency across time. Vertical dashed line show time period this standard was in service (1993-01-07 – 2001-08-09).



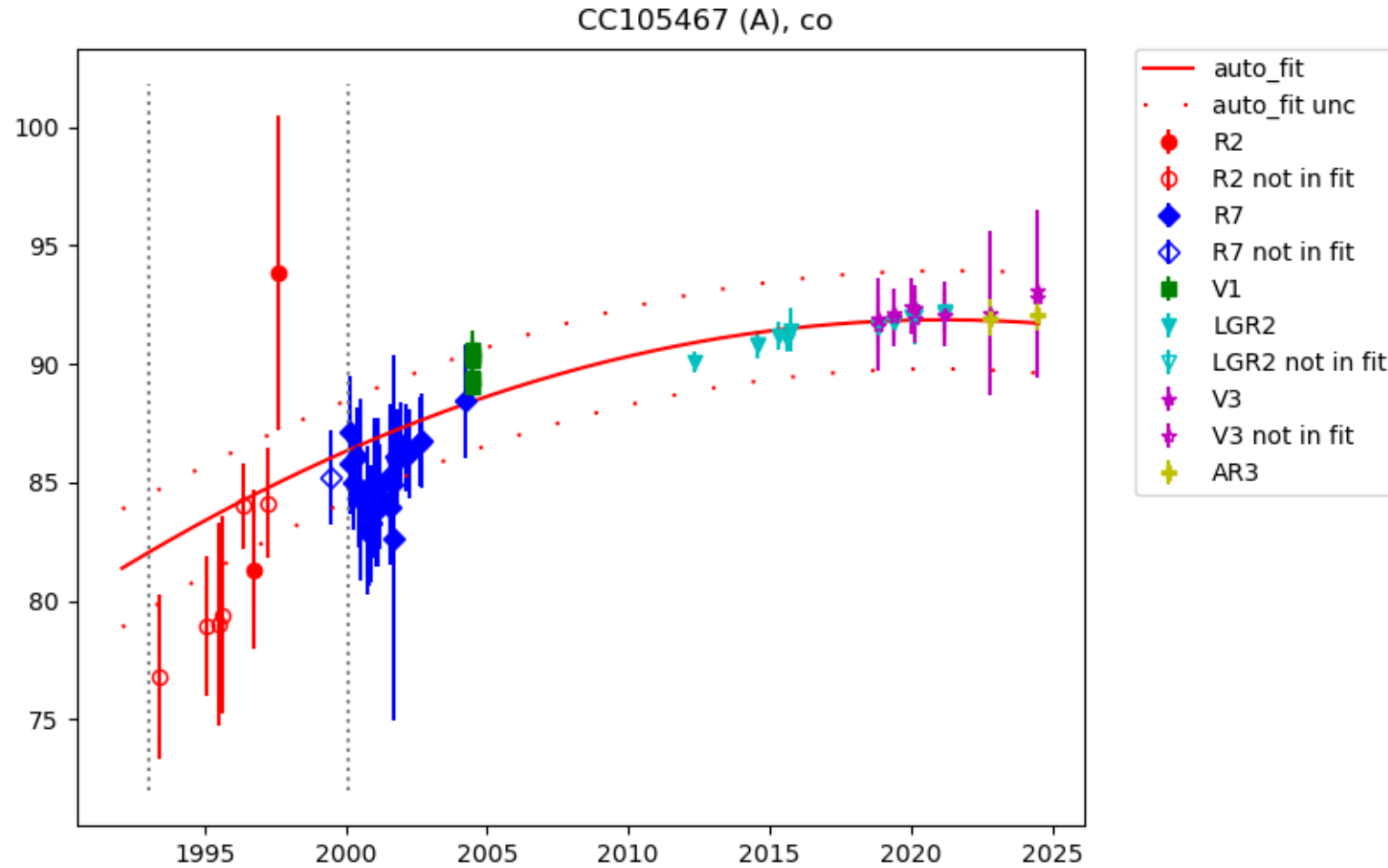
Secondary standards used on RGD2 system during 1990s

Filled symbols indicate independent measurements traceable to the scale. Open symbols indicate measurements relative to other secondary standards. These were not used to value assign the standards since they are not independent. However, they do help to show consistency across time. Vertical dashed line show time period this standard was in service (1993-03-09 – 2000-01-26).



Secondary standards used on RGD2 system during 1990s

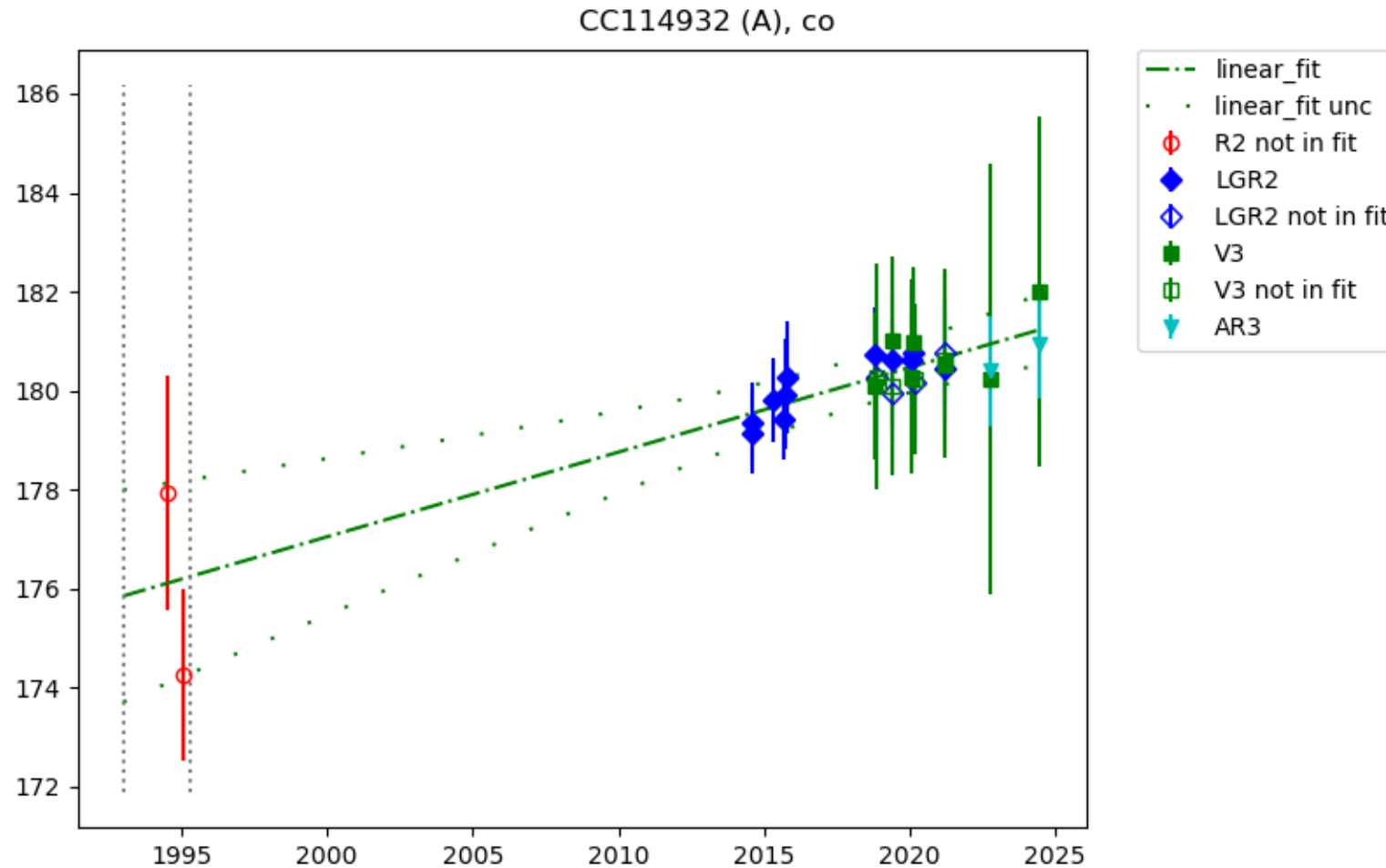
Filled symbols indicate independent measurements traceable to the scale. Open symbols indicate measurements relative to other secondary standards. These were not used to value assign the standards since they are not independent. However, they do help to show consistency across time. Vertical dashed line show time period this standard was in service (1993-01-07 – 2000-01-26).



Secondary standards used on RGD2 system during 1990s

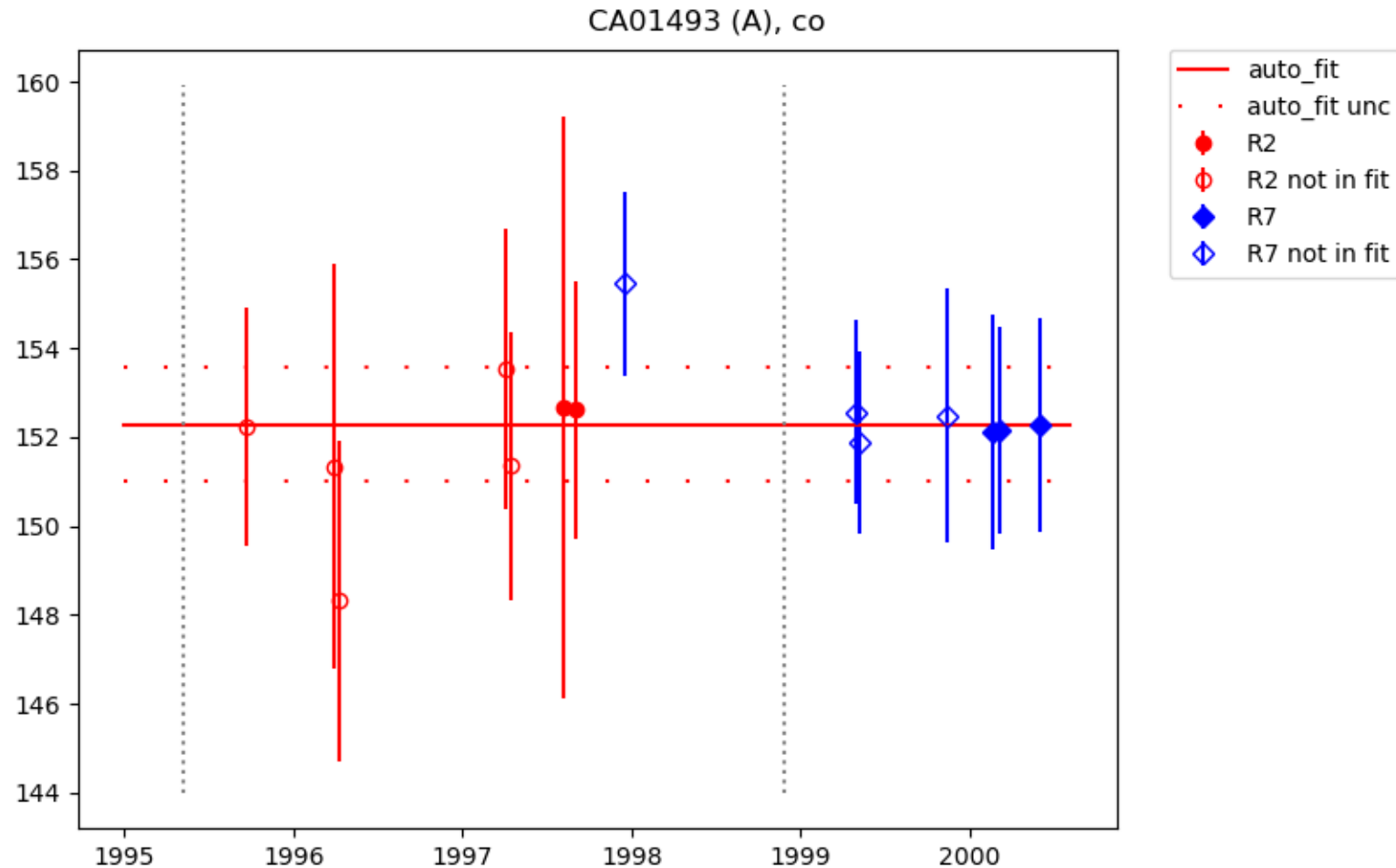
Filled symbols indicate independent measurements traceable to the scale. Open symbols indicate measurements relative to other secondary standards. These were not used to value assign the standards since they are not independent. However, they do help to show consistency across time. Vertical dashed line show time period this standard was in service (1993-01-07 – 1995-04-26).

Force linear fit for this standard.



Secondary standards used on RGD2 system during 1990s

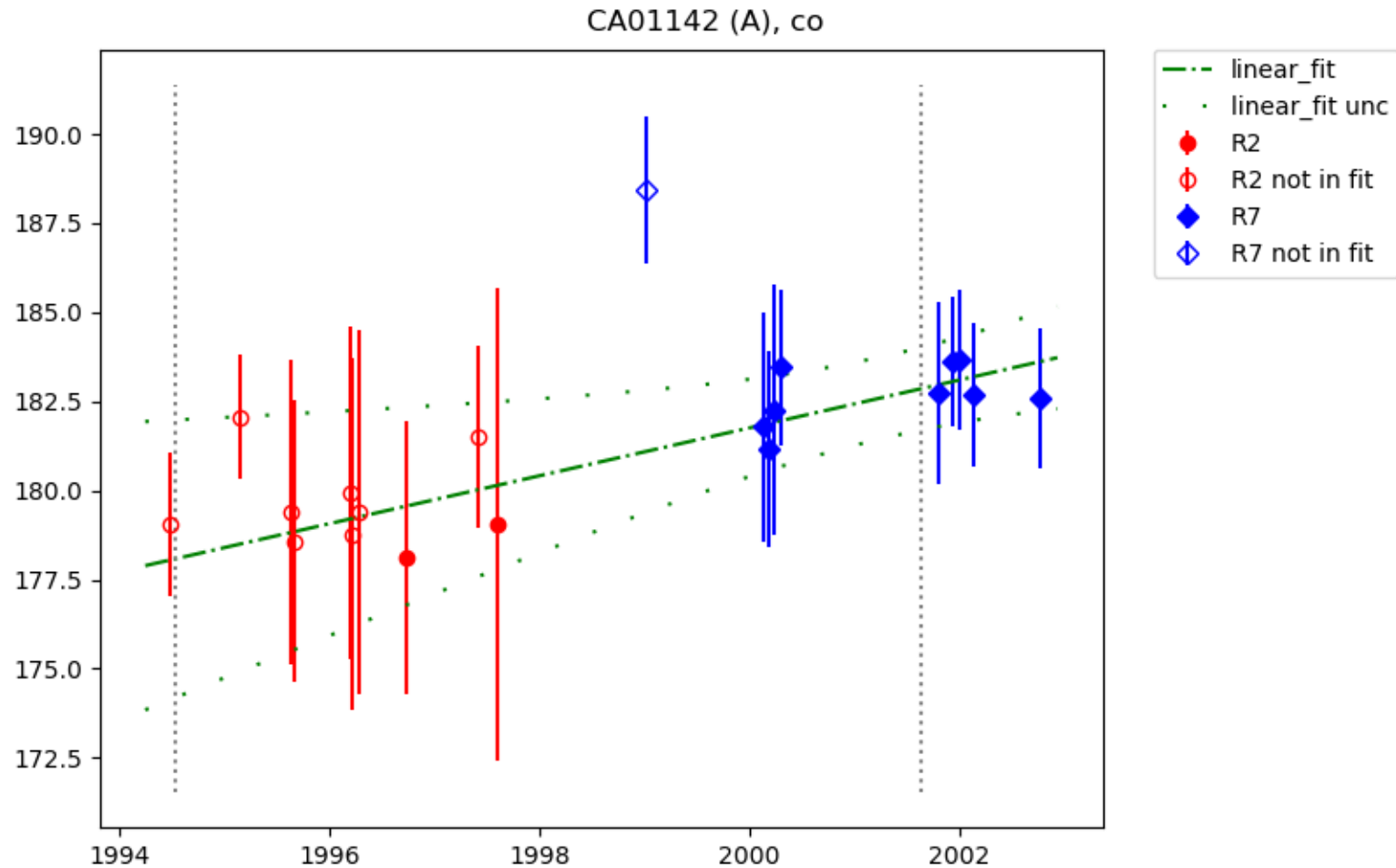
Filled symbols indicate independent measurements traceable to the scale. Open symbols indicate measurements relative to other secondary standards. These were not used to value assign the standards since they are not independent. However, they do help to show consistency across time. Vertical dashed line show time period this standard was in service (1995-05-08 – 1998-11-26).



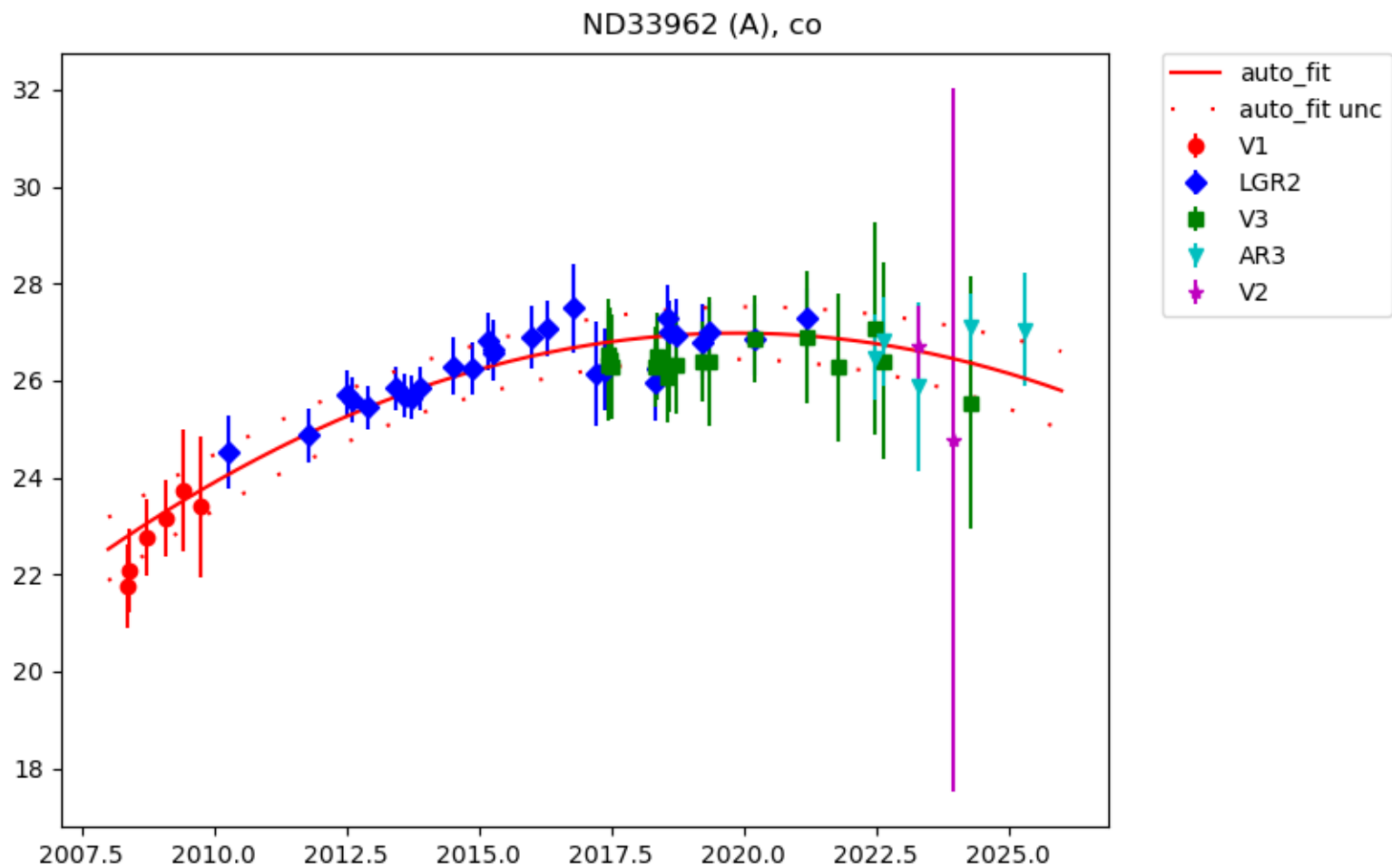
Secondary standards used on RGD2 system during 1990s

Filled symbols indicate independent measurements traceable to the scale. Open symbols indicate measurements relative to other secondary standards. These were not used to value assign the standards since they are not independent. However, they do help to show consistency across time. Vertical dashed line show time period this standard was in service (1994-07-14 – 2001-08-22).

Force linear fit for this standard.

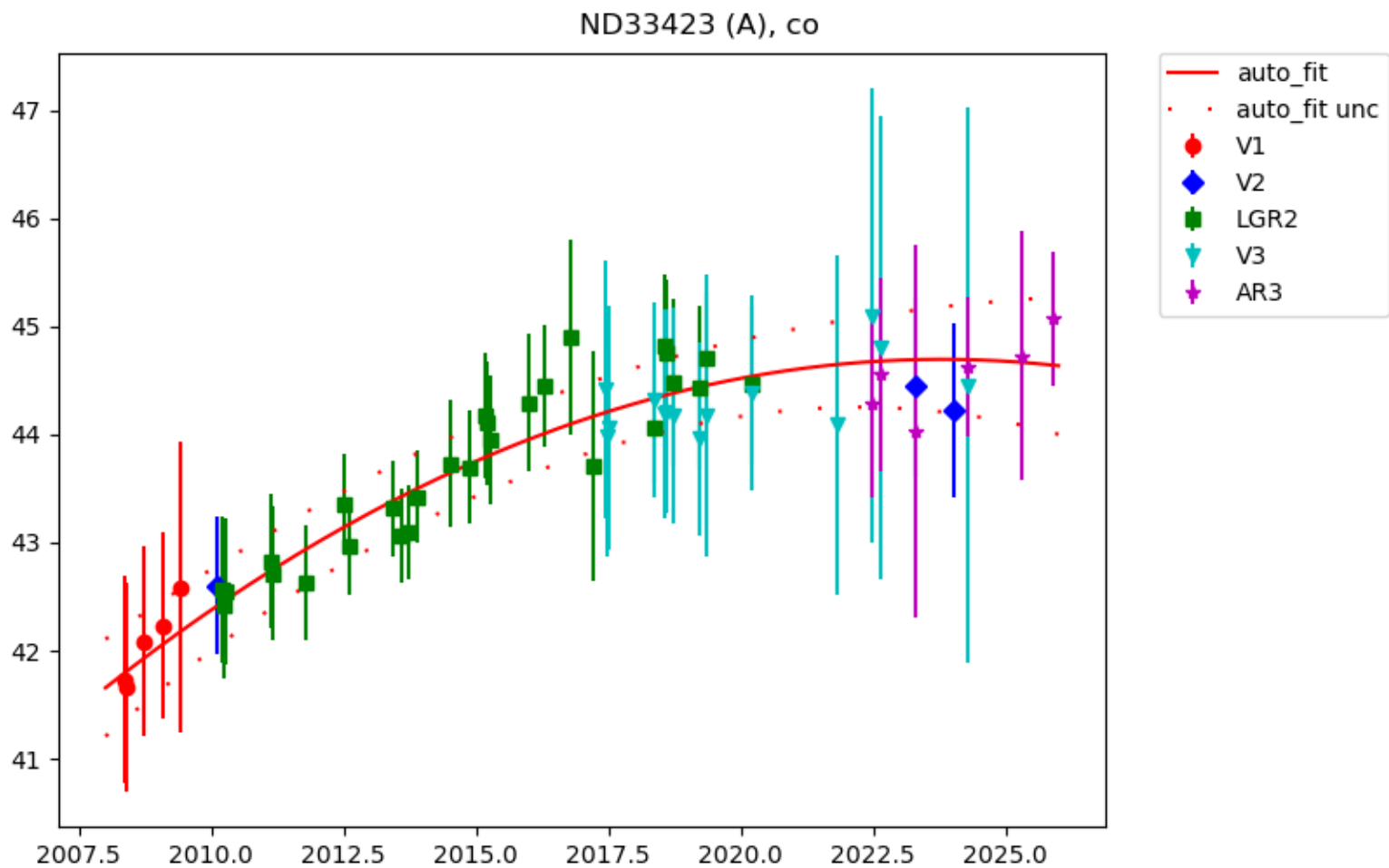


Long term target tanks. All measurements shown are at the tertiary level of the calibration hierarchy. R7 and early V1 data are vs 1999/2000 grav's. This is considered equivalent to the tertiary level because the 1999/2000 primary standards also served as working standards on R7 and V1. Later V1 data and all subsequent instruments are vs secondary standards. The current secondary standards went into service mid-2011.



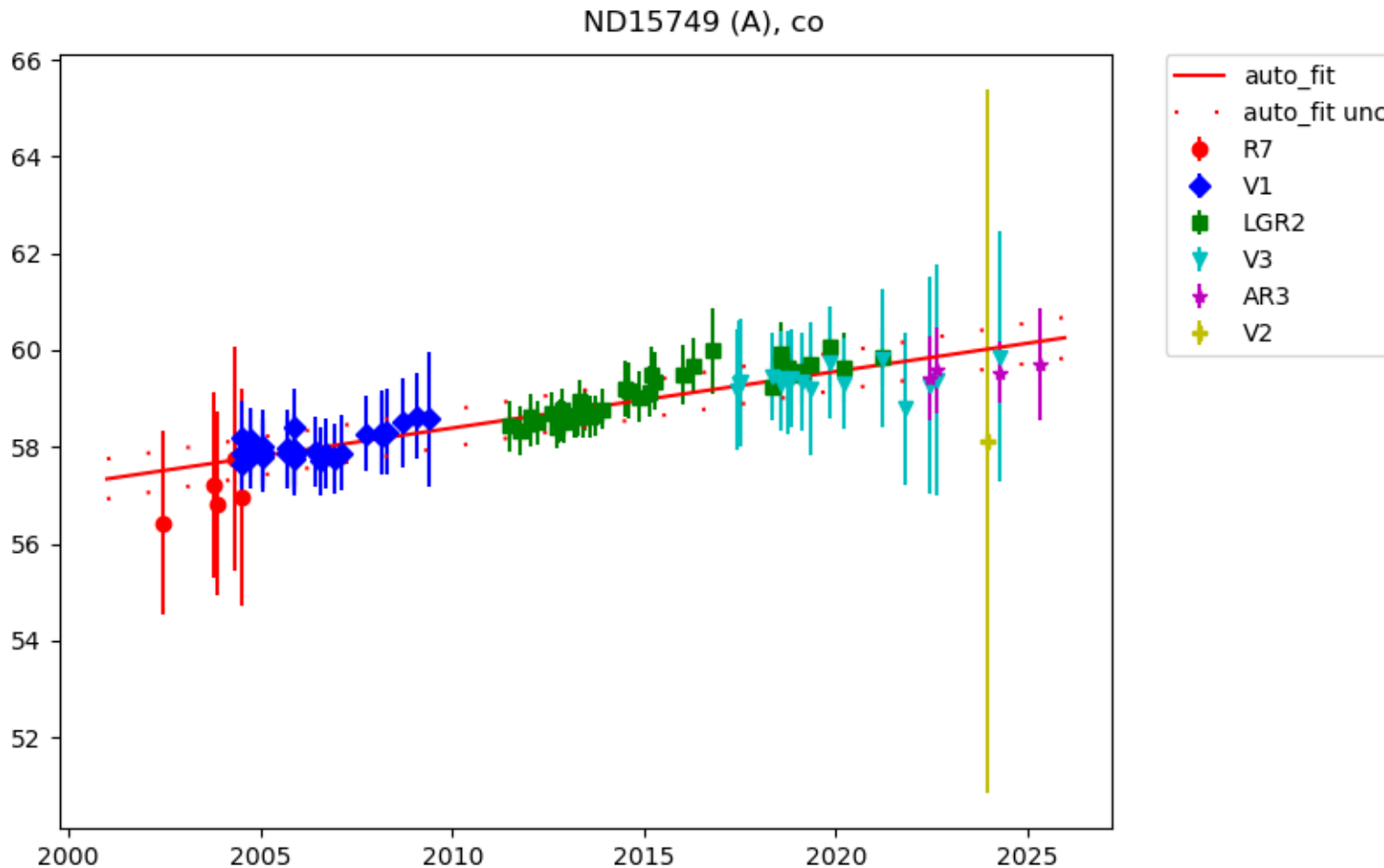
Serial_Number	Gas	Fill_Code	Time_Zero	Coef0	Coef1	Coef2	Unc_Coef0	Unc_Coef1	Unc_Coef2	Rsd	N	Chisq	Level
ND33962	co	A	2015.84976	26.470	0.25439	-0.03163	0.122	0.02601	0.00540	0.51	58	0.34	Tertiary

Long term target tanks. All measurements shown are at the tertiary level of the calibration hierarchy. R7 and early V1 data are vs 1999/2000 grav's. This is considered equivalent to the tertiary level because the 1999/2000 primary standards also served as working standards on R7 and V1. Later V1 data and all subsequent instruments are vs secondary standards. The current secondary standards went into service mid-2011.



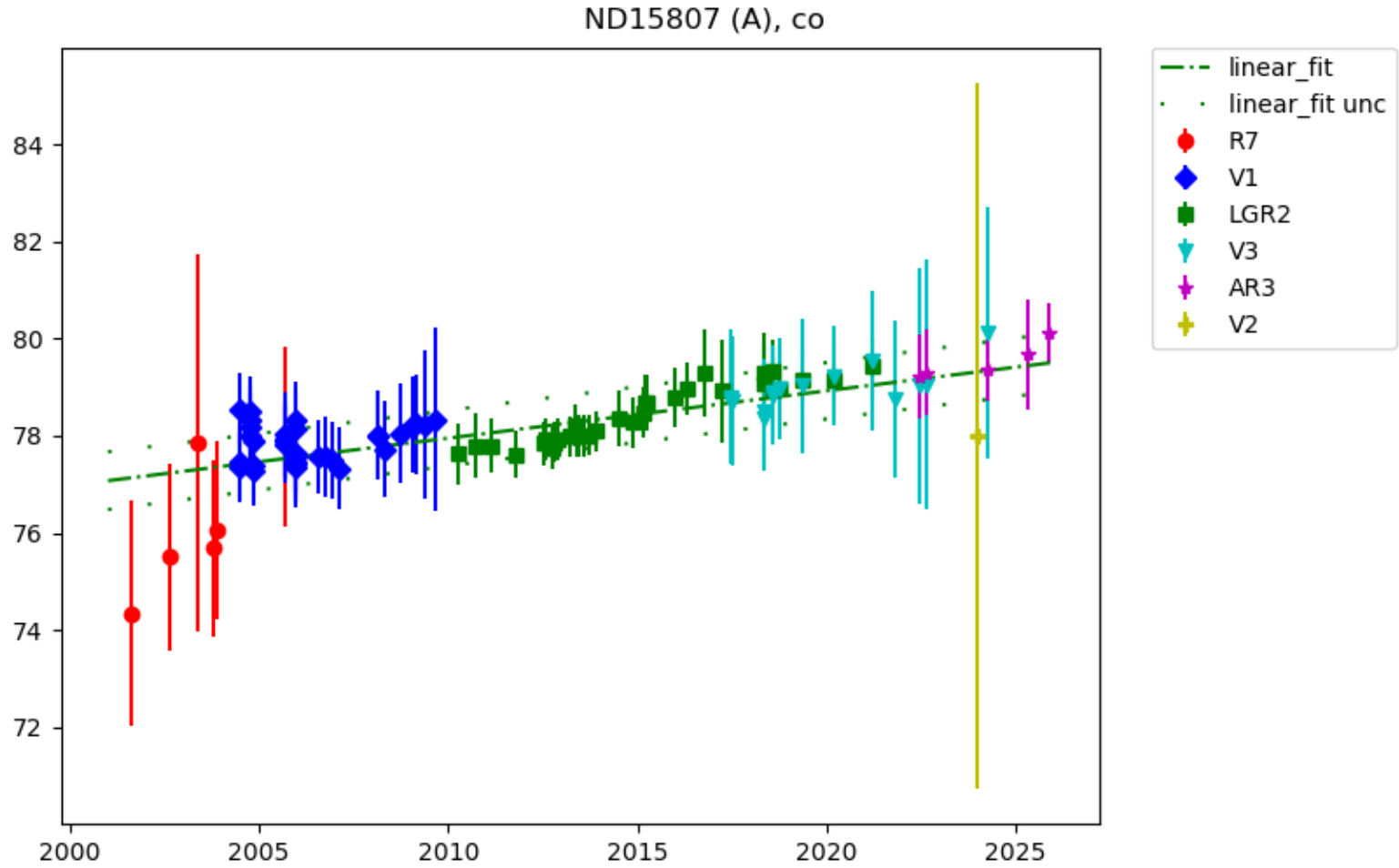
Serial_Number	Gas	Fill_Code	Time_Zero	Coef0	Coef1	Coef2	Unc_Coef0	Unc_Coef1	Unc_Coef2	Rsd	N	Chisq	Level
ND33423	co	A	2015.54751	43.867	0.20092	-0.01219	0.121	0.02460	0.00441	0.30	56	0.16	Tertiary

Long term target tanks. All measurements shown are at the tertiary level of the calibration hierarchy. R7 and early V1 data are vs 1999/2000 grav's. This is considered equivalent to the tertiary level because the 1999/2000 primary standards also served as working standards on R7 and V1. Later V1 data and all subsequent instruments are vs secondary standards. The current secondary standards went into service mid-2011.



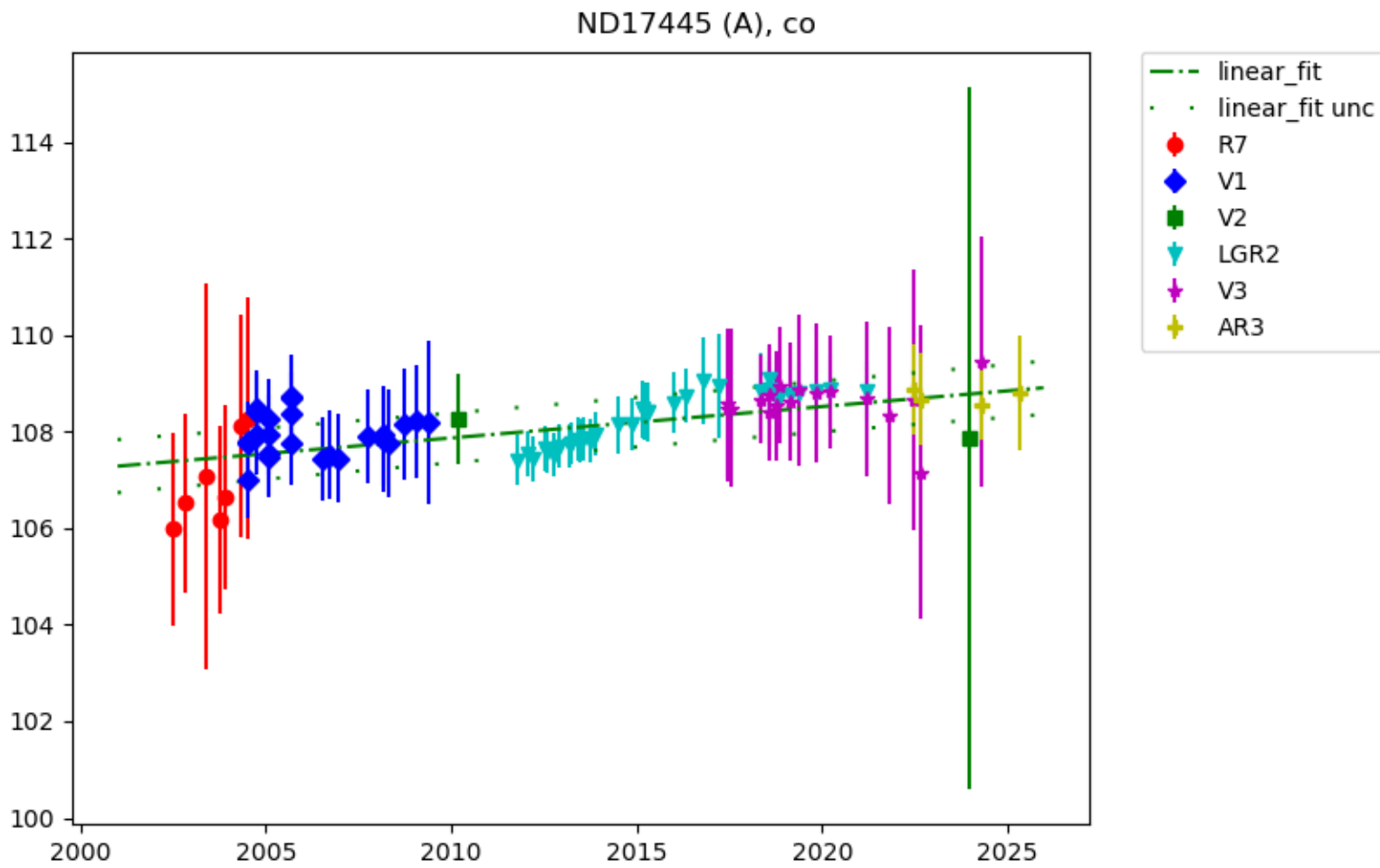
Serial_Number	Gas	Fill_Code	Time_Zero	Coef0	Coef1	Coef2	Unc_Coef0	Unc_Coef1	Unc_Coef2	Rsd	N	Chisq	Level
ND15749	co	A	2012.80895	58.720	0.11677	0.00000	0.067	0.01419	0.00000	0.37	96	0.14	Tertiary

Long term target tanks. All measurements shown are at the tertiary level of the calibration hierarchy. R7 and early V1 data are vs 1999/2000 grav's. This is considered equivalent to the tertiary level because the 1999/2000 primary standards also served as working standards on R7 and V1. Later V1 data and all subsequent instruments are vs secondary standards. The current secondary standards went into service mid-2011.



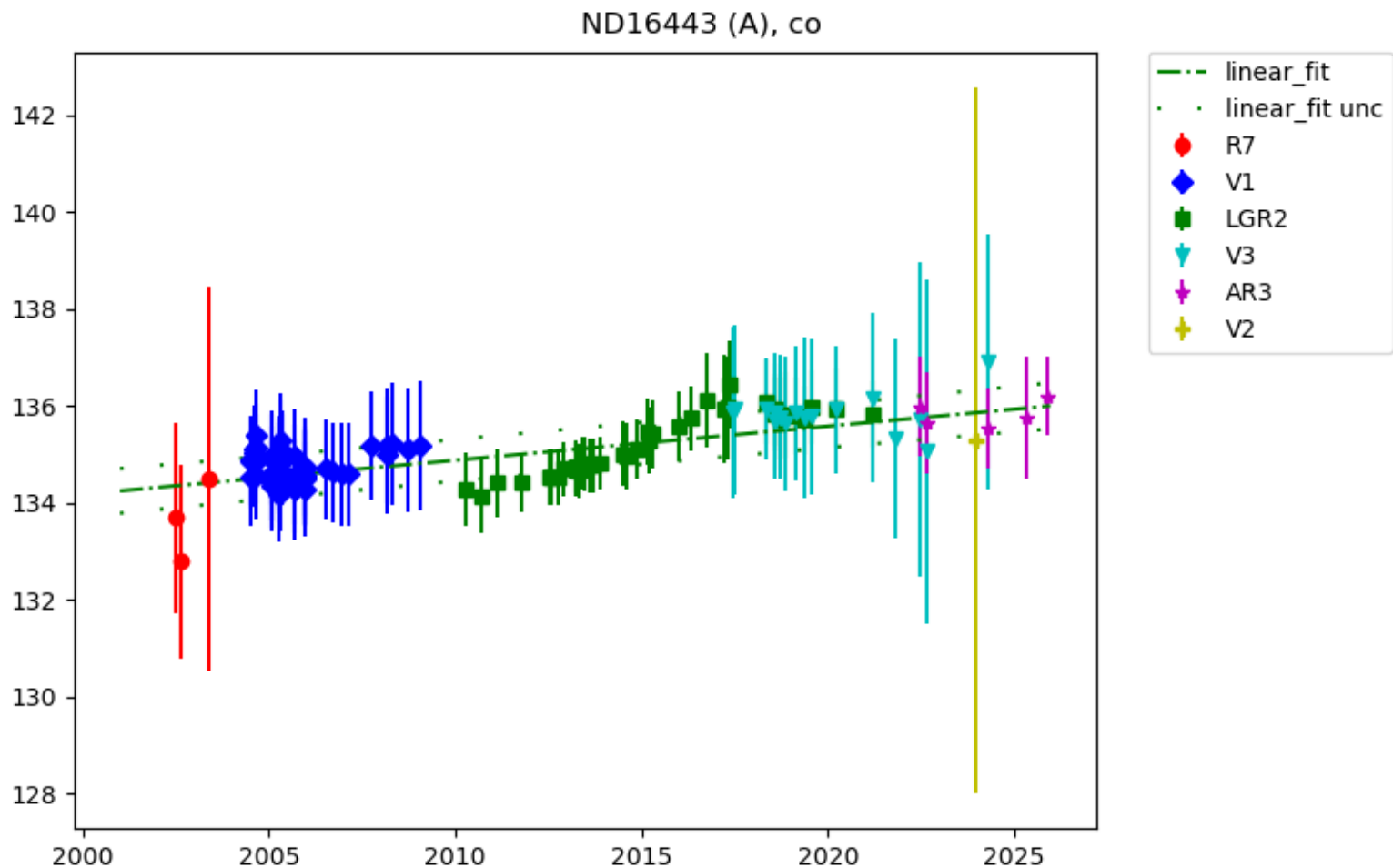
Serial_Number	Gas	Fill_Code	Time_Zero	Coef0	Coef1	Coef2	Unc_Coef0	Unc_Coef1	Unc_Coef2	Rsd	N	Chisq	Level
ND15807	co	A	2012.73040	78.215	0.09739	0.00000	0.073	0.01400	0.00000	0.57	93	0.31	Tertiary

Long term target tanks. All measurements shown are at the tertiary level of the calibration hierarchy. R7 and early V1 data are vs 1999/2000 grav's. This is considered equivalent to the tertiary level because the 1999/2000 primary standards also served as working standards on R7 and V1. Later V1 data and all subsequent instruments are vs secondary standards. The current secondary standards went into service mid-2011.



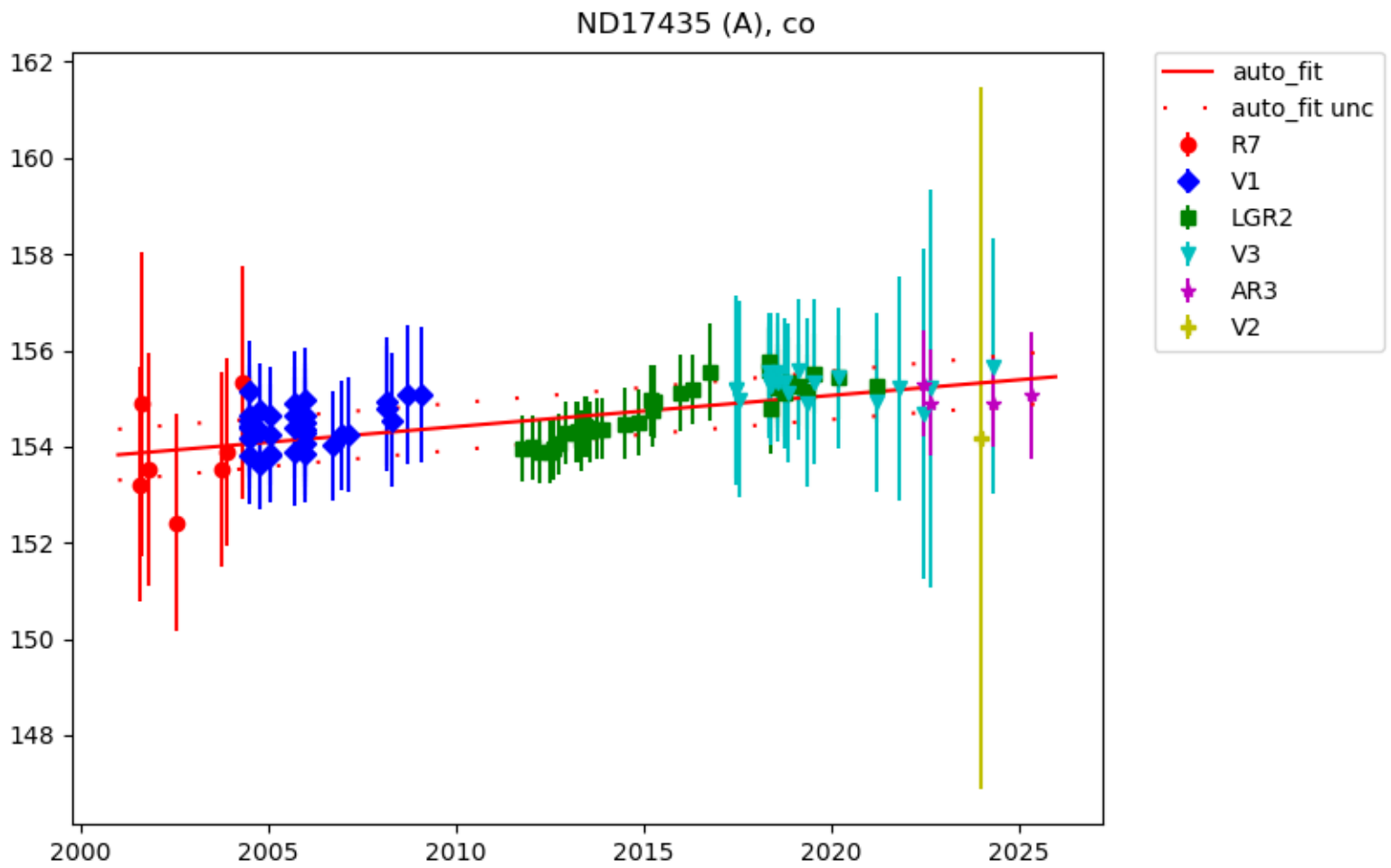
Serial_Number	Gas	Fill_Code	Time_Zero	Coef0	Coef1	Coef2	Unc_Coef0	Unc_Coef1	Unc_Coef2	Rsd	N	Chisq	Level
ND17445	co	A	2013.30088	108.086	0.06506	0.00000	0.079	0.01637	0.00000	0.51	89	0.32	Tertiary

Long term target tanks. All measurements shown are at the tertiary level of the calibration hierarchy. R7 and early V1 data are vs 1999/2000 grav's. This is considered equivalent to the tertiary level because the 1999/2000 primary standards also served as working standards on R7 and V1. Later V1 data and all subsequent instruments are vs secondary standards. The current secondary standards went into service mid-2011.



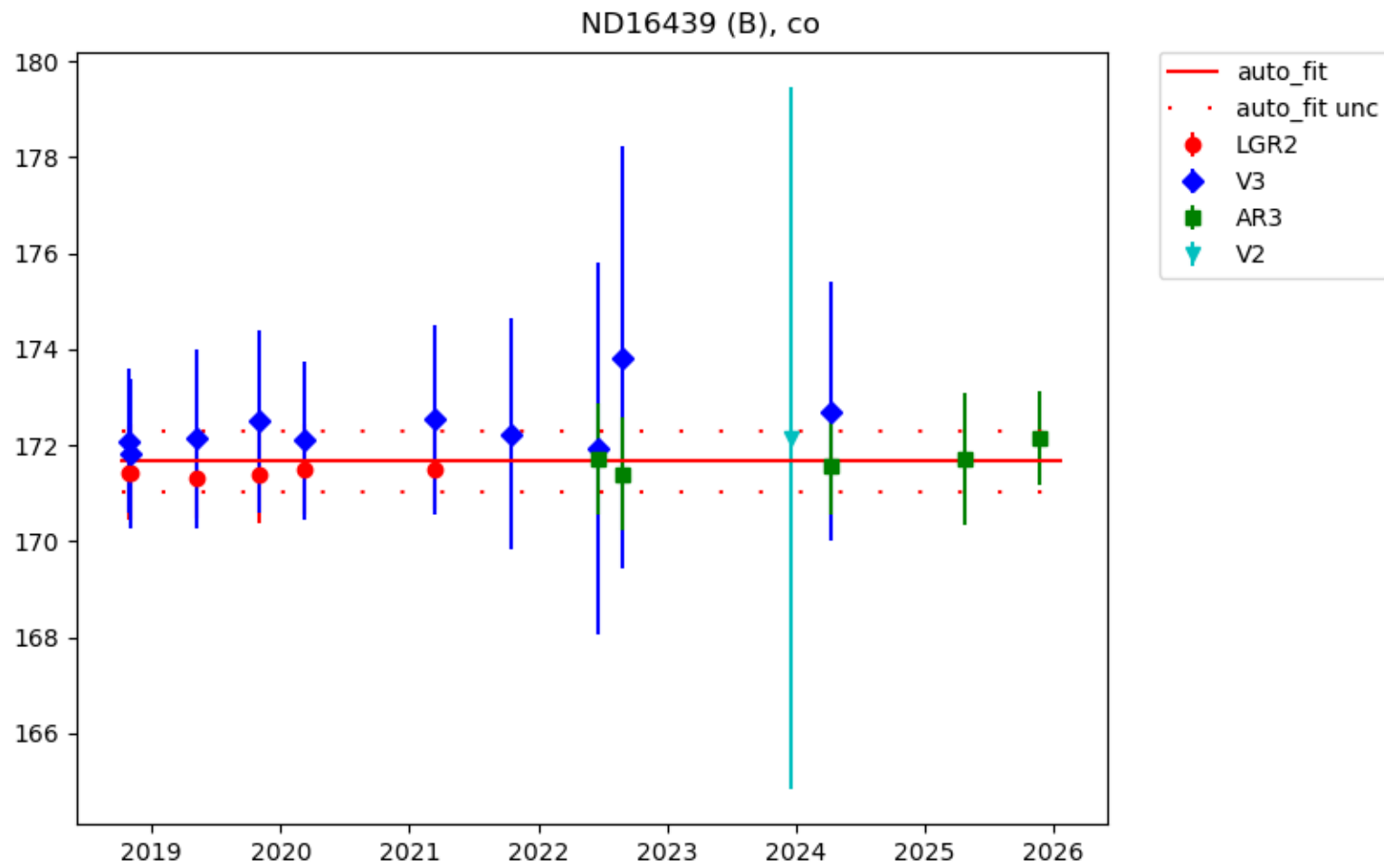
Serial_Number	Gas	Fill_Code	Time_Zero	Coef0	Coef1	Coef2	Unc_Coef0	Unc_Coef1	Unc_Coef2	Rsd	N	Chisq	Level
ND16443	co	A	2012.14689	135.028	0.07022	0.00000	0.082	0.01467	0.00000	0.42	112	0.22	Tertiary

Long term target tanks. All measurements shown are at the tertiary level of the calibration hierarchy. R7 and early V1 data are vs 1999/2000 grav's. This is considered equivalent to the tertiary level because the 1999/2000 primary standards also served as working standards on R7 and V1. Later V1 data and all subsequent instruments are vs secondary standards. The current secondary standards went into service mid-2011.

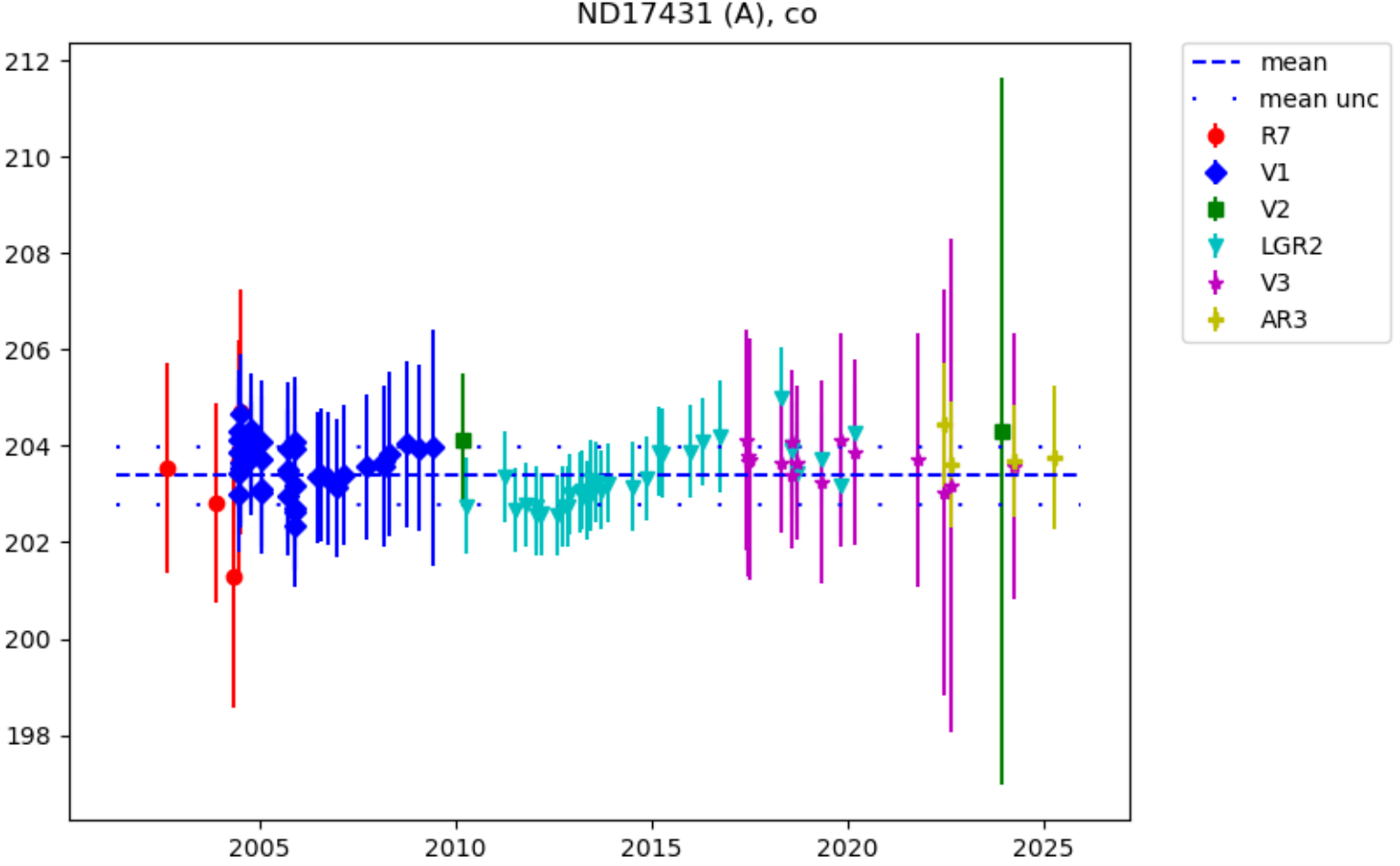


Serial_Number	Gas	Fill_Code	Time_Zero	Coef0	Coef1	Coef2	Unc_Coef0	Unc_Coef1	Unc_Coef2	Rsd	N	Chisq	Level
ND17435	co	A	2013.03000	154.612	0.06495	0.00000	0.096	0.01785	0.00000	0.48	100	0.21	Tertiary

Long term target tanks. All measurements shown are at the tertiary level of the calibration hierarchy. R7 and early V1 data are vs 1999/2000 grav's. This is considered equivalent to the tertiary level because the 1999/2000 primary standards also served as working standards on R7 and V1. Later V1 data and all subsequent instruments are vs secondary standards. The current secondary standards went into service mid-2011.

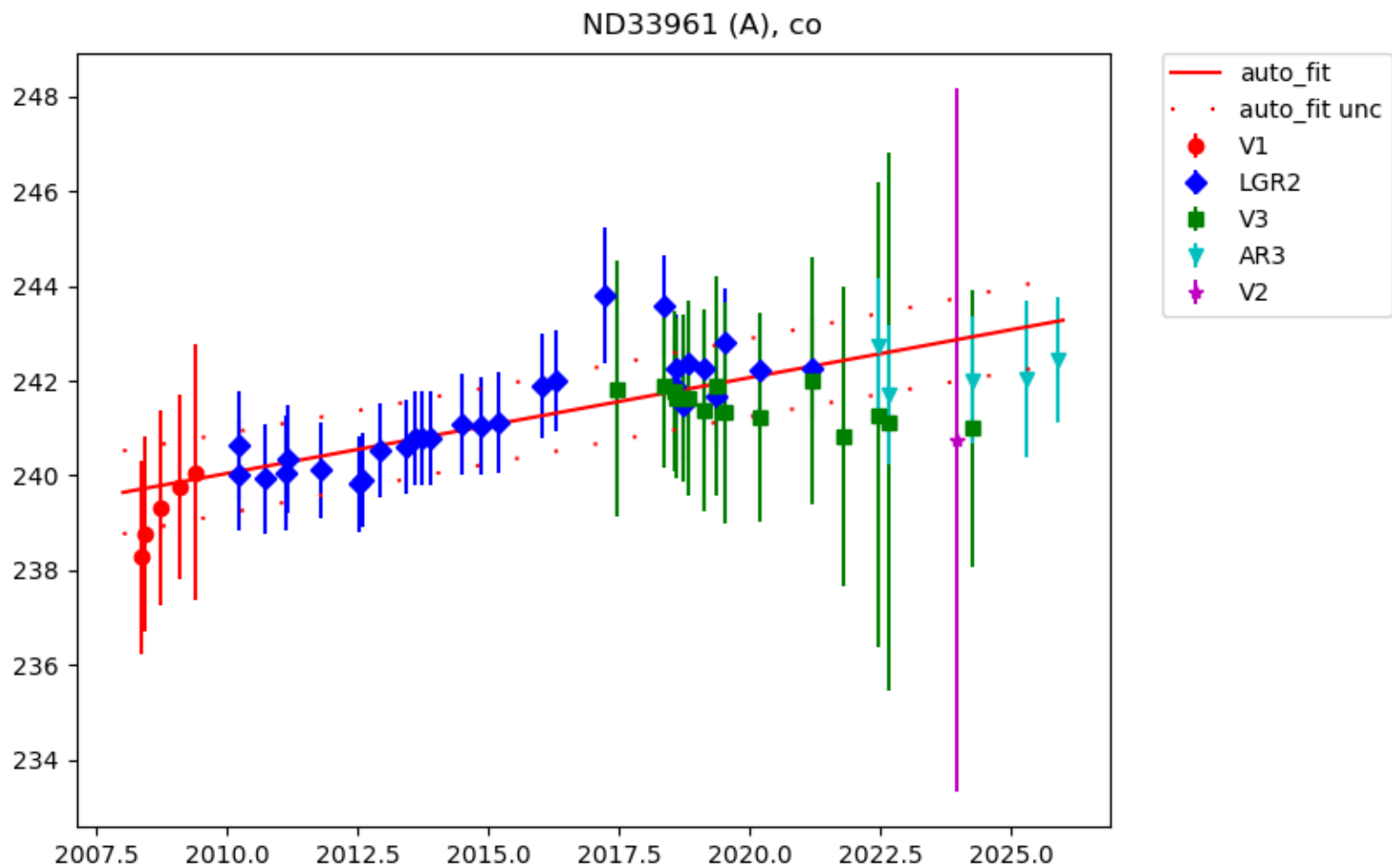


Long term target tanks. All measurements shown are at the tertiary level of the calibration hierarchy. R7 and early V1 data are vs 1999/2000 grav's. This is considered equivalent to the tertiary level because the 1999/2000 primary standards also served as working standards on R7 and V1. Later V1 data and all subsequent instruments are vs secondary standards. The current secondary standards went into service mid-2011.



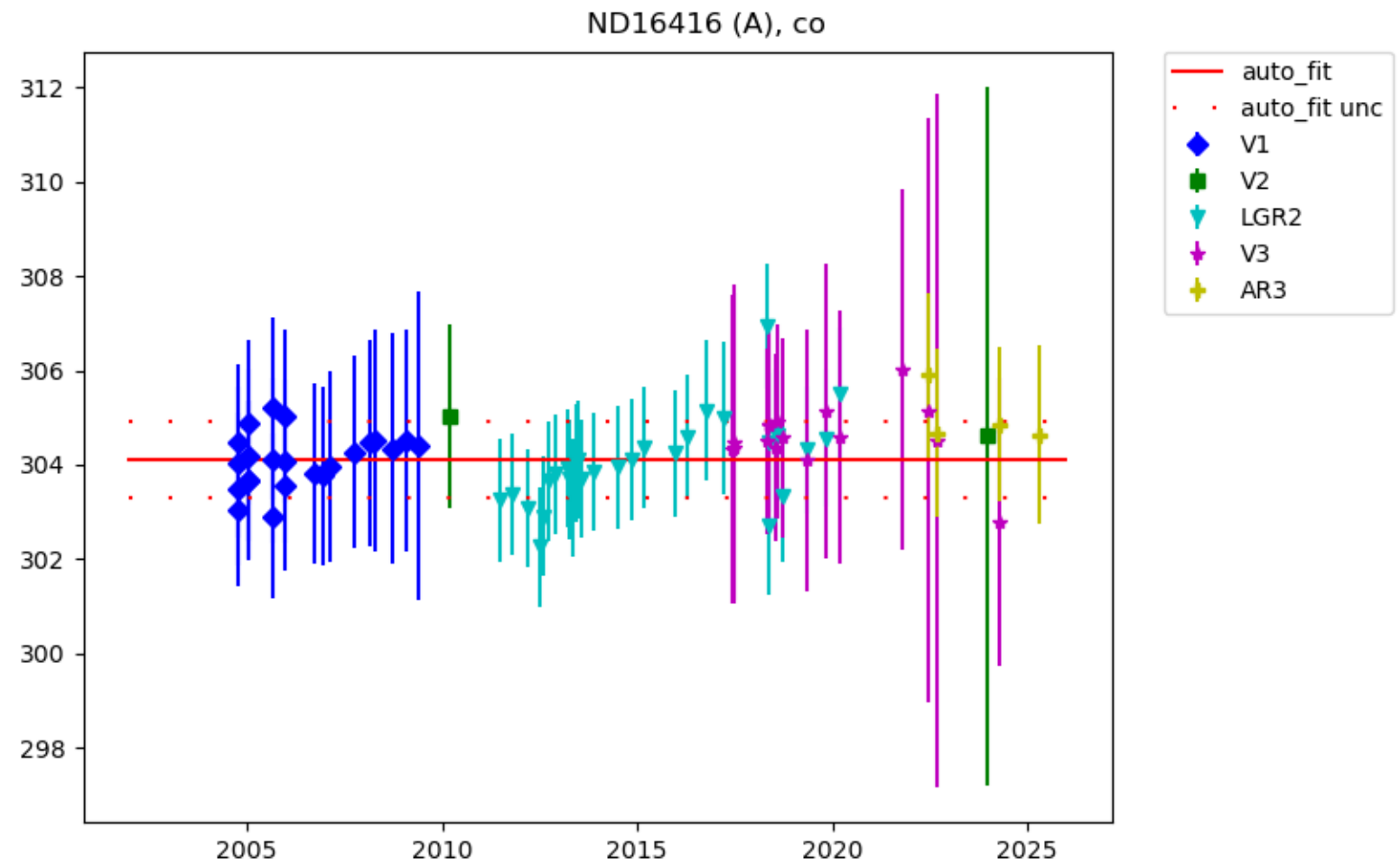
Serial_Number	Gas	Fill_Code	Time_Zero	Coef0	Coef1	Coef2	Unc_Coef0	Unc_Coef1	Unc_Coef2	Rsd	N	Chisq	Level
ND17431	co	A	2012.02310	203.397	0.00000	0.00000	0.120	0.00000	0.00000	0.59	97	0.23	Tertiary

Long term target tanks. All measurements shown are at the tertiary level of the calibration hierarchy. R7 and early V1 data are vs 1999/2000 grav's. This is considered equivalent to the tertiary level because the 1999/2000 primary standards also served as working standards on R7 and V1. Later V1 data and all subsequent instruments are vs secondary standards. The current secondary standards went into service mid-2011.



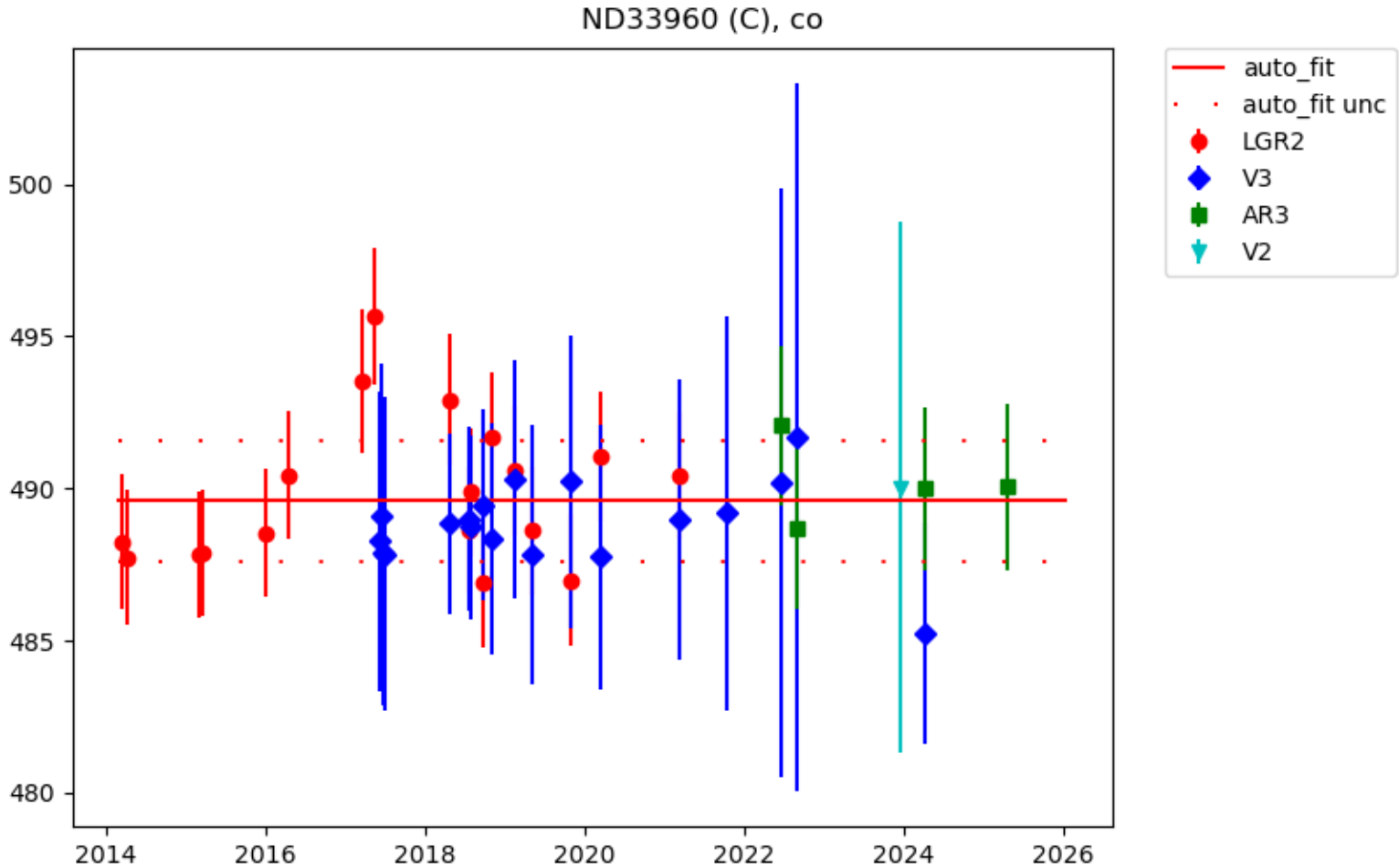
Serial_Number	Gas	Fill_Code	Time_Zero	Coef0	Coef1	Coef2	Unc_Coef0	Unc_Coef1	Unc_Coef2	Rsd	N	Chisq	Level
ND33961	co	A	2016.05001	241.269	0.20202	0.00000	0.180	0.04322	0.00000	0.78	55	0.24	Tertiary

Long term target tanks. All measurements shown are at the tertiary level of the calibration hierarchy. R7 and early V1 data are vs 1999/2000 grav's. This is considered equivalent to the tertiary level because the 1999/2000 primary standards also served as working standards on R7 and V1. Later V1 data and all subsequent instruments are vs secondary standards. The current secondary standards went into service mid-2011.



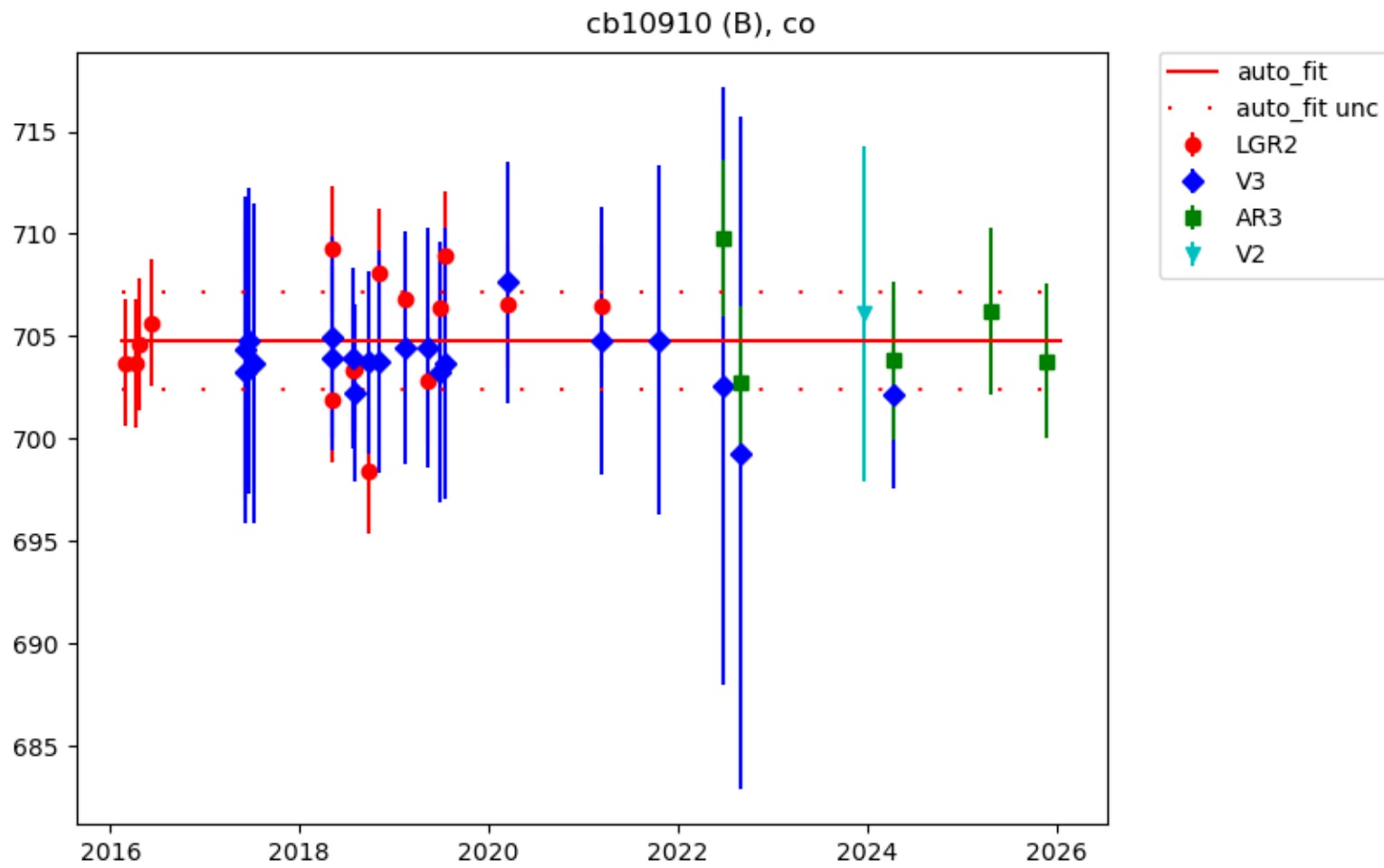
Serial_Number	Gas	Fill_Code	Time_Zero	Coef0	Coef1	Coef2	Unc_Coef0	Unc_Coef1	Unc_Coef2	Rsd	N	Chisq	Level
ND16416	co	A	2013.61744	304.116	0.00000	0.00000	0.190	0.00000	0.00000	0.79	75	0.25	Tertiary

Long term target tanks. All measurements shown are at the tertiary level of the calibration hierarchy. R7 and early V1 data are vs 1999/2000 grav's. This is considered equivalent to the tertiary level because the 1999/2000 primary standards also served as working standards on R7 and V1. Later V1 data and all subsequent instruments are vs secondary standards. The current secondary standards went into service mid-2011.



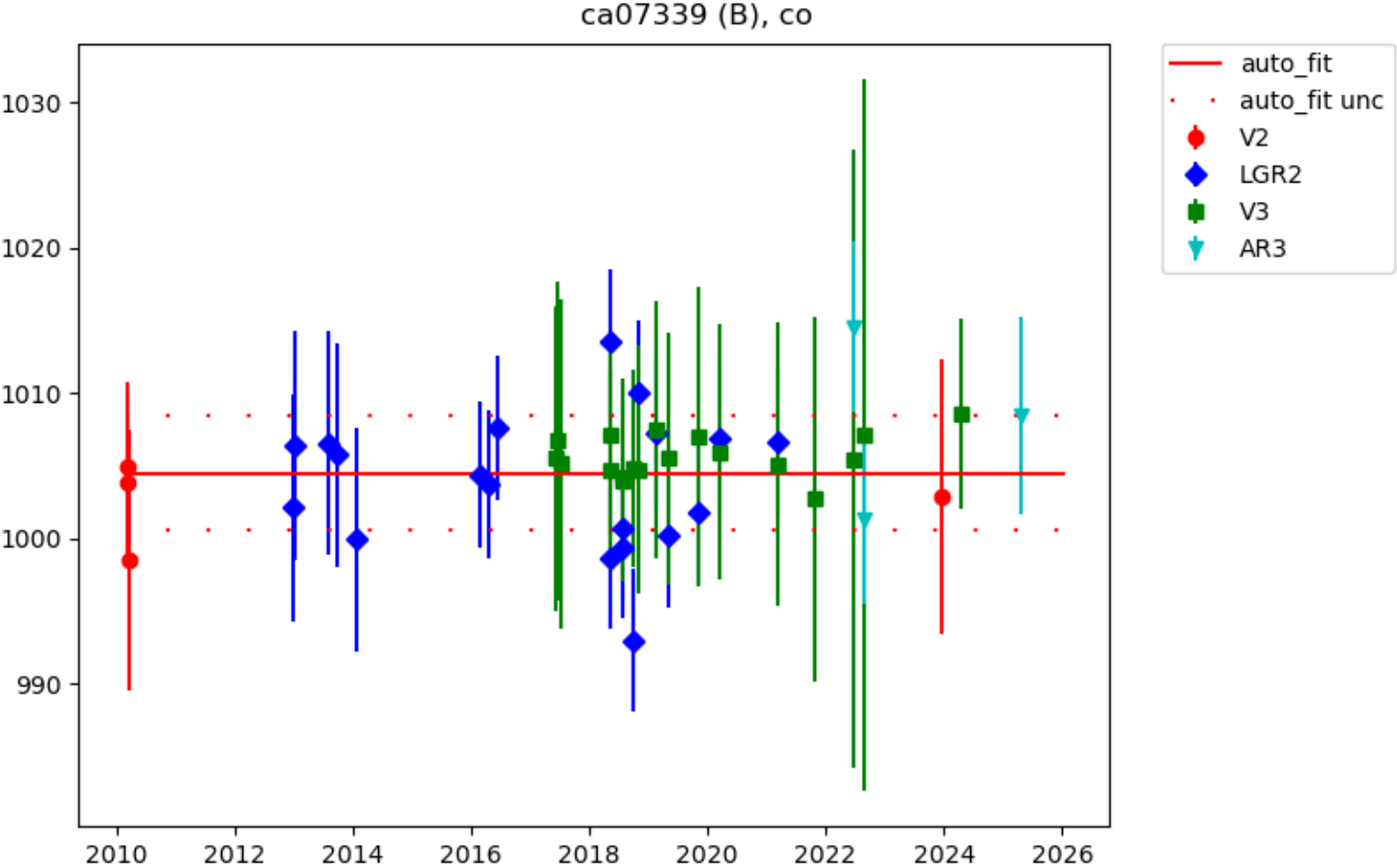
Serial_Number	Gas	Fill_Code	Time_Zero	Coef0	Coef1	Coef2	Unc_Coef0	Unc_Coef1	Unc_Coef2	Rsd	N	Chisq	Level
ND33960	co	C	2018.62358	489.603	0.00000	0.00000	0.425	0.00000	0.00000	1.94	41	0.60	Tertiary

Long term target tanks. All measurements shown are at the tertiary level of the calibration hierarchy. R7 and early V1 data are vs 1999/2000 grav's. This is considered equivalent to the tertiary level because the 1999/2000 primary standards also served as working standards on R7 and V1. Later V1 data and all subsequent instruments are vs secondary standards. The current secondary standards went into service mid-2011.



Serial_Number	Gas	Fill_Code	Time_Zero	Coef0	Coef1	Coef2	Unc_Coef0	Unc_Coef1	Unc_Coef2	Rsd	N	Chisq	Level
CB10910	co	B	2019.44292	704.789	0.00000	0.00000	0.621	0.00000	0.00000	2.31	42	0.40	Tertiary

Long term target tanks. All measurements shown are at the tertiary level of the calibration hierarchy. R7 and early V1 data are vs 1999/2000 grav's. This is considered equivalent to the tertiary level because the 1999/2000 primary standards also served as working standards on R7 and V1. Later V1 data and all subsequent instruments are vs secondary standards. The current secondary standards went into service mid-2011.

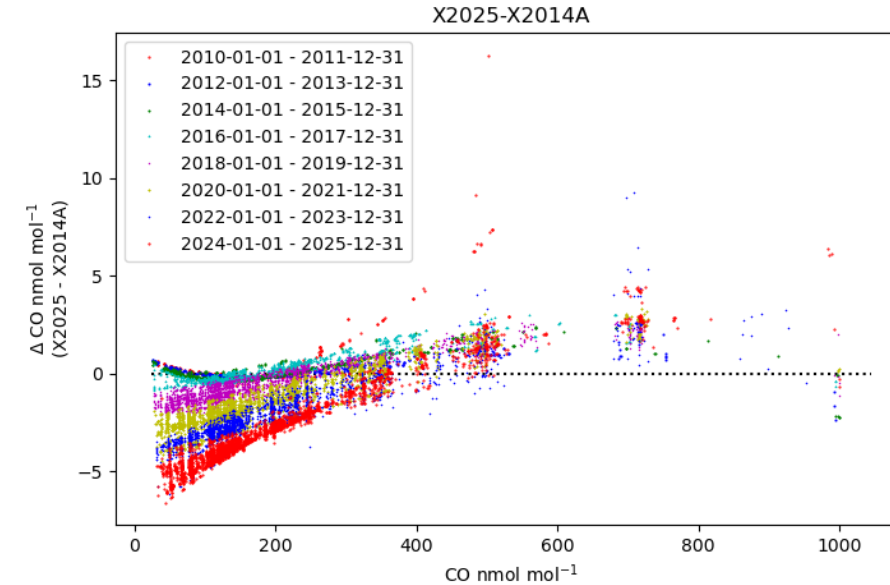


Serial_Number	Gas	Fill_Code	Time_Zero	Coef0	Coef1	Coef2	Unc_Coef0	Unc_Coef1	Unc_Coef2	Rsd	N	Chisq	Level
CA07339	co	B	2018.25018	1004.499	0.00000	0.00000	0.977	0.00000	0.00000	3.84	44	0.48	Tertiary

Bi-yearly, linear mole fraction relationships between X2014A and X2025. Years 2010 – 2025. Potential for these to be used when clear traceability exists during this time period.

For fits below:

meas_value = X2014A
y = calculated X2025 value



Fit results for ['rgd2', 'cocal-1'] vs calibration system

2010-01-01 - 2011-12-31 (linear): $Y = -0.088654 (0.028054) + 1.000324 (0.000173) * [\text{meas_value}]$ (sdresid: 1.413918 n: 534)

***** Range of unc values calculated from predictive interval of fit: Min 1.41 Max 1.43 (over mf range 23.8 - 1044.6)

2012-01-01 - 2013-12-31 (linear): $Y = -0.139331 (0.012054) + 1.000288 (0.000084) * [\text{meas_value}]$ (sdresid: 0.287135 n: 1219)

***** Range of unc values calculated from predictive interval of fit: Min 0.29 Max 0.30 (over mf range 23.8 - 1044.6)

2014-01-01 - 2015-12-31 (linear): $Y = -0.505586 (0.012777) + 1.002588 (0.000083) * [\text{meas_value}]$ (sdresid: 0.388687 n: 1561)

***** Range of unc values calculated from predictive interval of fit: Min 0.39 Max 0.40 (over mf range 23.8 - 1044.6)

2016-01-01 - 2017-12-31 (linear): $Y = -1.045736 (0.013800) + 1.006135 (0.000080) * [\text{meas_value}]$ (sdresid: 0.372882 n: 1419)

***** Range of unc values calculated from predictive interval of fit: Min 0.37 Max 0.43 (over mf range 23.8 - 1044.6)

2018-01-01 - 2019-12-31 (linear): $Y = -2.062754 (0.011017) + 1.007652 (0.000059) * [\text{meas_value}]$ (sdresid: 0.481270 n: 2799)

***** Range of unc values calculated from predictive interval of fit: Min 0.48 Max 0.50 (over mf range 23.8 - 1044.6)

2020-01-01 - 2021-12-31 (linear): $Y = -3.252271 (0.011371) + 1.010067 (0.000063) * [\text{meas_value}]$ (sdresid: 0.587580 n: 2544)

***** Range of unc values calculated from predictive interval of fit: Min 0.59 Max 0.61 (over mf range 23.8 - 1044.6)

2022-01-01 - 2023-12-31 (linear): $Y = -4.122461 (0.012104) + 1.010658 (0.000061) * [\text{meas_value}]$ (sdresid: 0.598962 n: 2198)

***** Range of unc values calculated from predictive interval of fit: Min 0.60 Max 0.65 (over mf range 23.8 - 1044.6)

2024-01-01 - 2025-12-31 (linear): $Y = -5.786450 (0.012966) + 1.014692 (0.000062) * [\text{meas_value}]$ (sdresid: 0.529862 n: 3014)

***** Range of unc values calculated from predictive interval of fit: Min 0.53 Max 0.58 (over mf range 23.8 - 1044.6)